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THE QUANTITATIVE SEPARATION AND DETERMINATION OF URANIUM.

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THE work described in this article was undertaken with the object of finding out the most accurate and satisfactory method for the technical estimation of uranium.

The usual quantitative methods for the estimation of uranium were first repeated, then new methods for its separation and estimation were tried on solutions containing known amounts of pure salts, and the best conditions for both separation and determination were carefully worked out.

The research was drawn to a close by making a number of assays of uraninite, in which the results obtained from the work on pure salt solutions were applied. These assays tested the methods on the most important ore of uranium, and thus collected the data in the form of analytical methods.

HISTORICAL INTRODUCTION.

Uranium was discovered by M. H. Klaproth, who separated what he thought to be a new element from pitchblende—also known as uraninite—the principal ore of uranium. This was in

1789, and what he obtained was not the element, but its lower oxide, UO_2. He named the element uranium in remembrance of the planet Uranus, which Herschel discovered in 1781.

From 1789 to 1795 much work was done on the investigation of uranium, but nothing new was discovered till 1840, when E. Péligot succeeded in isolating metallic uranium in powder form by heating uranous chloride (UCl_4) with metallic sodium.[1] He made a great number of experiments, the results of which proved that what was previously thought to be the element uranium was its lower oxide (UO_2), which plays the part of a base, a true inorganic radical. This discovery seems to have been an impetus to the further study of this element, as we find records in the different journals, of the years that follow, of several of the eminent chemists of the day investigating uranium and trying to find new methods for its estimation.

Clemens Zimmerman was the next chemist of note to investigate uranium. He studied methods for isolating the metal, and methods for its estimation and separation from other elements, and prepared many of its salts, studying their chemical and physical properties.[2] This work covered a number of years, from 1877 to 1884. So 1877 marks the second revival of interest in the element uranium. The first revival was in 1840, when Péligot isolated metallic uranium. The third revival is the present time, brought on by the great industrial demand for uranium ores.

In 1854 the only use to which uranium was put was for making a very fine black for porcelain painting,[3] and from 1850 to 1866 it was much used in photography. At present its uses are for the preparation of acetate and nitrate salts (which are used as chemical reagents), for the manufacture of a certain highly prized canary-yellow colored glass, for the preparation of a pigment used for porcelain painting, and lastly for making a steel which has properties superior to nickel steel.[4]

PART I.—SEPARATION OF URANIUM.

SEPARATION OF URANIUM FROM MEMBERS OF THE FIFTH AND SIXTH GROUPS.

The only point to be determined for the well-known separation

[1] *Ann. Chem.* (Liebig), **41**, 141 (1842).
[2] *Ibid.*, Vols. **119**, **204**, **213** and **214**.
[3] Whitney's "Mineral Wealth of the United States."
[4] *Moniteur Industrial*, **27**, 44 (1900).

by hydrogen sulphide was the exact acidity of the solution. This was done by mixing standardized solutions of lead, copper, and uranium in different proportions, and precipitating the lead and copper by hydrogen sulphide, under varying conditions of acidity and temperature. The experiments were all conducted quantitatively. These showed that a perfect separation was effected when 1 cc. of concentrated nitric acid (sp. gr. 1.42) was present to every 50 cc. of solution, and the solution saturated with hydrogen sulphide in the cold.

With hydrochloric acid, 1 cc. of concentrated acid (sp. gr. 1.20) to 50 cc. of solution gave excellent results. This amount must not be exceeded, as when 2.5 per cent. of concentrated acid was present the precipitation of the lead was incomplete. Less acid must be present if the precipitation is done from a hot solution, but this is not recommended.

As 5 cc. of concentrated acid in a bulk of 250 cc. solution gave a perfect separation of uranium from the metals of the fifth group, whose sulphides are the most soluble—lead and cadmium—and also from copper, these conditions must also be suitable for the other members of this group. Lead requires the least amount of free acid to retain it in solution ; then follow in order of succession, cadmium, mercury, bismuth, copper, and silver.[1]

SEPARATION OF VANADIUM FROM URANIUM.

Vanadium is one of the common associates of uranium, and especially so in the minerals which occur in Colorado. Carnotite, the most common of these minerals, has of late reached commercial importance.

The separation of vanadium from uranium presents very little difficulty unless phosphoric acid is present, in which case the separation is troublesome. Friedel and Cumenge[2] separated vanadium from uranium by evaporating the solution to dryness with nitric acid. The uranium was then extracted from the dry mass with a warm dilute solution of ammonium nitrate. For this separation, no phosphoric acid should be present as it renders the uranium oxide, with which it is combined, insoluble in the dilute ammonium nitrate solution.

The method for the separation of vanadium from iron by means

[1] Fresenius' "Quantitative Chemical Analysis," p. 456, 1900.

[2] *Am. J. Sci.*, **10**, 135 (1900).

of mercuric oxide and mercurous nitrate[1] has been used with success by A. C. Langmuir,[2] for the separation of vanadium from uranium in the analysis of carnotite. The finely divided mineral was dissolved in the smallest possible amount of nitric acid, and the silica filtered off. The solution was diluted to about 500 cc. and the vanadium precipitated by means of mercurous nitrate as follows: The nitric acid solution was nearly neutralized with pure yellow mercuric oxide, and the vanadium then precipitated by the addition of a strong solution of mercurous nitrate. The solution was brought to boiling, after which it was filtered. (If chromium, tungsten, or molybdenum are present they go down as mercurous salts with the mercurous vanadate.) The precipitate was washed with a warm dilute solution of mercurous nitrate, after which it was dried, ignited, and weighed as V_2O_5. The excess of mercury in the filtrate was removed by means of hydrogen sulphide gas. After expelling the hydrogen sulphide from the filtrate by slow boiling, the uranium was determined by the ordinary method.

O. P. Fritchie's Method[3] is said to be particularly adapted to the mineral carnotite. The finely divided mineral was decomposed at boiling temperature with 10 cc. nitric acid, taken up with 10 cc. water, neutralized with a saturated solution of sodium carbonate, added 5 cc. in excess, and 20 cc. of a 20 per cent. sodium hydroxide solution; it was boiled slowly for half an hour, and the precipitate allowed to settle. The vanadium, uranium, and iron were all precipitated by the sodium carbonate, but on adding a moderate excess and a large excess of sodium hydroxide, the vanadium was dissolved while the uranium and iron remained insoluble. Uranium is easily precipitated by sodium carbonate and sodium hydroxide in the presence of an iron salt. The precipitate was washed with a solution of sodium hydroxide. The uranium and iron were then separated by the ordinary method, and each determined volumetrically by means of standard permanganate, after reducing their sulphate solutions at boiling temperature with metallic aluminum.

SEPARATION OF URANIUM FROM MEMBERS OF THE THIRD AND FOURTH GROUPS, PARTICULARLY IRON.

The methods ordinarily used for separating uranium from the

[1] Blair's "Chemical Analysis of Iron," 3rd edition, p. 200.
[2] Paper read before N. Y. Section of American Chemical Society, at March meeting.
[3] *Eng. Min. J.*, Nov. 10, 1900; *Chem. News*, **82**, 258 (1900).

other members of the fourth group and those of the third group depends on the solubility of uranium hydroxide and sulphide in an excess of a strong solution of an alkali carbonate. The hydroxides and sulphides of the other members of these two groups are, with the exception of iron and nickel, insoluble in alkali carbonate solutions. The hydroxides of these two metals are only slightly soluble in strong alkali carbonate solutions; in cold dilute solutions they are almost insoluble.

The element which gives the most trouble in effecting a separation from uranium is iron. A great number of methods have been proposed, of which the best known are Pisani's ammonium carbonate[1] and Patera's sodium carbonate[2] methods, neither of which are very satisfactory. Rose used ammonium carbonate followed by ammonium sulphide,[3] thus precipitating the iron. This latter method is far from satisfactory, especially if the uranium is small in amount. Rheineck's basic acetate method[4] has been used with success when the uranium was present in considerable quantity.

Ether Separation.—The use of ether to effect a separation of iron from uranium was suggested by A. C. Langmuir in a recent article[5] on the analysis of nickel ores. He found that iron could be separated from copper, manganese, aluminum, cobalt, nickel, and zinc, by taking advantage of the solubility of ferric chloride in ether free from alcohol. The chlorides of the other metals are not taken up by the ether but remain in the aqueous hydrochloric acid solution. When iron is in the ferrous condition, Rothe[6] found that it was not taken into solution by the ether, but remained with the other metals in the aqueous solution. So it is necessary to oxidize the iron before attempting to make the separation.

EXPERIMENTAL.

The separation of iron from uranium by means of ether was tried, and, as the result, a clean and rather rapid separation has been worked out. This separation depends on the complete extraction of ferric chloride (in an aqueous hydrochloric acid solu-

[1] *Compt. rend.*, **52**, 106.
[2] *Zischr. anal. Chem.*, **5**, 228 (1866).
[3] *Ibid.*, **1**, 410 (1862).
[4] *Chem. News*, **24**, 233 (1871).
[5] This Journal, **22**, 102 (1900).
[6] *Chem. News*, **66**, 182.

tion) by ether which is free from alcohol, and the retention of uranyl chloride in the aqueous hydrochloric acid solution.

Before undertaking the separation of iron from uranium by means of ether, two solutions containing uranium alone were treated three times with ether, as described in the following experiments, in order to test the solubility of uranyl chloride in ether. These experiments showed uranyl chloride to be entirely insoluble in ethyl ether which is free from alcohol.

The experiments which follow were made with solutions containing both uranium and iron. Measured amounts of a standard uranium nitrate solution and of a standard ferric chloride solution were placed in a small beaker and the solution twice evaporated to dryness with 10 cc. hydrochloric acid (sp. gr. 1.20). The dry mass was taken up with about 10 cc. dilute hydrochloric acid (sp. gr. 1.10) and heated till all salts were dissolved, but not long enough to lose any of the acid by volatilization. After the solution had cooled, it was poured into a 250 cc. separatory funnel and the beaker rinsed out with dilute hydrochloric acid (sp. gr. 1.10). The rinsings were added to the separatory funnel till the volume of the solution had reached 50 cc. Fifty cc. of ether, free from alcohol and previously shaken up with hydrochloric acid (sp. gr. 1.10), were added and agitated for about ten minutes, occasionally relieving the pressure in the funnel. After thoroughly shaking together, the two solutions were allowed to separate and the lower aqueous hydrochloric acid solution of uranyl chloride, containing some iron, was drawn off catching it in another separatory funnel. The ether solution of ferric chloride was washed twice with 10 cc. dilute hydrochloric acid (sp. gr. 1.10) and the washings, after allowing to separate, were run into the funnel containing the uranium.

On determining the amount of iron extracted from the hydrochloric acid solution by the ether, it was found that all the iron was not separated from the uranium by one extraction, about 10.5 per cent. of the amount taken remaining in the aqueous solution with the uranium.

On finding that all of the iron was not separated from the uranium by one "ether extraction," two extractions were made on a solution containing 0.1155 gram uranium and 0.0901 gram of iron. The first extraction was made in the same manner as outlined above, and the second as follows: The solution in the lower

separatory funnel was again shaken for about seven minutes with 50 cc. ether. After thoroughly shaking together, the two solutions were allowed to separate, and the lower aqueous hydrochloric acid layer run into a second funnel. The ether solution was twice washed with 10 cc. hydrochloric acid (sp. gr. 1.10), and the washings caught in the second funnel. The ether solution was run into a beaker which contained the ether from the first extraction. After distilling off the ether, the iron was determined by titration with 0.01 normal potassium permanganate solution. About 3.5 per cent. of the iron taken remained in the aqueous solution with the uranium.

The next five separations of iron from uranium were made by using hydrochloric acid of about 1.10 specific gravity (1 part acid (sp. gr. 1.20) and 1 part distilled water). In all cases three "ether extractions" were made, whereby practically complete separations of iron from uranium were obtained. The solutions contained from 0.0901 to 0.1802 gram iron and from 0.0962 to 0.2310 gram uranium. The amount of metal in their respective solutions was determined volumetrically, and did not vary more than 0.3 per cent. of the theoretical amounts taken.

The next five experiments were made by varying the strength of the hydrochloric acid used. The procedure was the same as above, making three extractions with ether. For the first three solutions, hydrochloric acid of about 1.133 specific gravity (2 parts acid (sp. gr. 1.20) and 1 part distilled water) was used; and for the last two solutions hydrochloric acid of about 1.066 specific gravity (1 part acid (sp. gr. 1.20), and 2 parts distilled water). The separation in both cases, of iron from uranium, was incomplete. When hydrochloric acid of 1.133 specific gravity was used, the amount of iron remaining with the uranium, after three "ether extractions," was about 6 per cent. of the amount taken. With hydrochloric acid of 1.066 specific gravity, the amount of iron which remained with the uranium after three "ether extractions," was about 25 per cent. of the amount taken.

The most complete separations of iron from uranium by means of ether are evidently obtained by using hydrochloric acid of 1.10 specific gravity. This is the same strength as was found by Speller[1] to be the best for the separation of iron from copper, manganese, aluminum, chromium, cobalt, and nickel.

[1] *Chem. News*, **83**, 124 (1901).

When rather concentrated hydrochloric acid (sp. gr. 1.133) was used for the solution of the chlorides of iron and uranium, it was noticed that on diluting the aqueous solution, after agitating with ether, quite an amount of ether separated. This seems to explain the reason why iron is not readily separated from uranium by means of ether when strong hydrochloric acid is used to bring their chlorides into solution, the iron being retained by the large quantity of ether which remains with the acid solution.

The results obtained are shown in the following table:

SEPARATION OF IRON FROM URANIUM BY EXTRACTION WITH ETHER.

Experiment No.	Specific gravity of HCl used.	Volume of solution at first extraction. cc.	Number of ether extractions made.	Ether used for			Theoretical amt of uranium taken.	Amount of uranium determined in aqueous HCl solution.	Theoretical amt of iron taken.	Amount of iron determined in ethereal extract.
				First extraction. cc.	Second extraction. cc.	Third extraction. cc.				
1	1.10	40	3	50	40	40	0.09625	0.09588	.....	.....
2	1.133	40	3	50	40	40	0.09625	0.09643	.....	.....
3	1.10	50	1	50	..	..	0.11550	0.13171	0.09010	0.08415
4	1.10	50	1	50	..	..	0.11550	0.14700	0.09010	0.07700
5	1.10	50	2	50	50	..	0.11550	0.12466	0.09010	0.08690
6	1.10	40	3	50	50	50	0.09625	0.09643	0.09010	0.08993
7	1.10	25	3	75	50	35	0.11550	0.11525	0.09010	0.09020
8	1.10	25	3	75	50	35	0.09625	0.09643	0.18021	0.18029
9	1.10	25	3	75	50	35	0.19250	0.19228	0.09010	0.08993
10	1.10	25	3	75	50	35	0.23099	0.23069	0.09010	0.09037
11	1.133	40	3	50	50	50	0.09625	0.10584	0.09010	0.08663
12	1.133	25	3	75	50	35	0.11550	0.12068	0.09010	0.08580
13	1.133	25	3	75	50	35	0.19250	0.20815	0.09010	0.08250
14	1.066	25	3	75	50	35	0.09625	0.20933	0.18022	0.12705
15	1.066	25	3	75	50	35	0.23099	0.27224	0.09010	0.07150

SEPARATION OF URANIUM FROM COBALT, NICKEL, AND ZINC.

Wolcott Gibbs separated uranium from cobalt, nickel, and zinc by means of hydrogen sulphide. He states that this method is much simpler than those ordinarily used, and also gave excellent results.[1] To the neutral or nearly neutral solution of the chlorides of uranium, cobalt, nickel, and zinc, add sodium acetate in excess and a few drops of acetic acid. The solution is boiled, and a rapid current of hydrogen sulphide passed through the boiling solution for half an hour. Every trace of the cobalt, nickel, and zinc is precipitated as sulphides while the whole of the uranium, and

[1] Silliman's *Am. J. Sci. and Art*, [2], **39**, 62 (1865).

any manganese, if present, remains in the boiling solution. The precipitate is thrown on a ribbed filter and quickly washed with cold hydrogen sulphide water. The precipitate is easily washed, and though the sulphides of cobalt and nickel formed in this manner are more easily oxidized than when precipitated by sodium sulphide from a boiling solution, they will be found to present no difficulty as regards oxidation upon the filter. If manganese is in the filtrate it may be determined by boiling with hydrochloric acid and precipitating it in the usual manner with sodium carbonate. The uranium in the filtrate is determined by the ordinary method.

Rose separated uranium from cobalt, nickel, and zinc by means of barium carbonate.[1] The precipitation of the uranium is complete from uranic solutions which contain a small amount of free acid, either hydrochloric or nitric acid. Barium carbonate, which is diffused in water, is added in excess and the solution allowed to stand twenty-four hours. The presence of ammonium chloride is necessary in order to keep the cobalt, nickel, and zinc in solution. The uranium is separated from the excess of barium carbonate by dissolving the precipitate in hydrochloric acid, and adding dilute sulphuric acid. The uranium in the filtrate is precipitated with ammonia, and weighed as oxide. C. Rammelsberg[2] employed this method to separate uranium from cobalt and nickel and obtained excellent results; but when manganese and zinc are present it cannot be advantageously employed.

SEPARATION OF URANIUM FROM THE ALKALI AND THE ALKALINE EARTH METALS.

If a solution containing uranium, alkalies, and alkaline earths is precipitated with ammonia, a portion of the alkalies and alkaline earths is carried down by the ammonium uranate,[3] thus preventing a complete separation.

Hillebrand[4] found that it is possible to completely separate uranium from the alkalies and alkaline earths by several precipitations with ammonia. In order to verify this statement, solutions containing a measured amount of standard uranium nitrate solution and sodium and potassium salts were precipitated by

[1] Rose's "Chimie Analytique—Analyse Quantitative," p. 248, (1862.)
[2] *Chem. Centrbl.* (1884), p. 806.
[3] Fresenius' "Quantitative Chemical Analysis," 6th edition, p. 533.
[4] *Am. J. Sci.*, **10**, 136 (1900).

means of a slight excess of ammonia, and the solutions brought to boiling. The precipitates were washed with a warm 2 per cent. solution of ammonium chloride, after which they were dissolved from the filters with warm hydrochloric acid (sp. gr. 1.10) and caught in beakers. The precipitation of the uranium by ammonia, in the presence of ammonium chloride and from hot solutions, was repeated twice, and it was found that after three precipitations the ammonium uranate was free from alkalies.

Magnesium may be separated from uranium by means of ammonium sulphide in the presence of ammonium chloride[1] and also by ammonia in the presence of an excess of ammonium chloride. The latter method is the one ordinarily used.[2] To the solution containing uranium and magnesium, add ammonium chloride and boil. When the solution becomes clear, add a slight excess of ammonia to the hot solution and continue boiling for a few minutes. Filter while hot and wash the precipitate with hot water containing ammonium chloride. Dry, ignite, and weigh the uranium as oxide.

The separation of uranium from barium, strontium, and calcium is usually done by means of sulphuric acid in the presence of alcohol.[3] The metals should be in solution as chlorides, having present the smallest possible amount of free hydrochloric acid. To the moderately dilute solution, add sulphuric acid, then alcohol, which precipitates the barium, strontium, and calcium, in the form of sulphates. The uranium in the filtrate is precipitated with ammonia and weighed as oxide.

The separation of uranium from barium, strontium, and calcium, may be brought about by precipitating the uranium with freshly prepared ammonium sulphide (free from carbon dioxide).[4]

In 1885, G. Alibigoff studied the action of mercuric oxide on uranium solutions and found a means of separating uranium from the alkalies and alkaline earths.[5] He showed that neither ammonium sulphide, nor ammonium carbonate followed by ammonium oxalate, can be successfully employed for separating uranium from calcium. The latter method is, however, preferable to the first. He states that a com-

[1] *Zischr. anal. Chem.*, **4**, 384 (1865).
[2] Fremy's "Encyclopédie Chimique, p. 86, (1884).
[3] *Ibid*, p. 86, (1884).
[4] Fresenius' "Quantitative Chemical Analysis," p. 534.
[5] *Ann. Chem.* (Liebig), **233**, 147 (1886).

plete separation of uranium from calcium, strontium, magnesium and the alkalies can be effected by the use of mercuric oxide; it does not, however, afford a separation of uranium from barium. The precipitation is made by adding a slight excess of freshly prepared mercuric oxide (in the form of an emulsion) to the boiling solution which contains ammonium chloride or nitrate. The boiling is continued for a few minutes longer and then rapidly cooled by placing the vessel into cold water. Wash the precipitate by decantation with a cold dilute solution of ammonium chloride. It is placed along with the filter in a platinum crucible, cautiously heated at first, after which the temperature is gradually raised and finally ignited over a blast-lamp. The residue consists of pure U_3O_8. The separation of uranium from the alkali metals by this method does not give any undue trouble, but when calcium and strontium are present they are rather hard to rid from the uranium precipitate. This difficulty is overcome by boiling several times, during washing by decantation, with a solution of ammonium chloride and each time rapidly cooling the solution before pouring off the supernatant liquid. The calcium and strontium in the filtrate are determined by the ordinary methods after the removal of the mercury by hydrogen sulphide.

SEPARATION OF URANIUM FROM THE ALKALI AND ALKALINE EARTH METALS BY ELECTROLYSIS OF ACETATE SOLUTION.

Uranium is a very difficult metal to separate from the alkalies and alkaline earths by gravimetric methods; but by electrolyzing an acetate solution of these elements a perfect separation can be effected[1]. It can be readily separated from sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, and barium. This method was used by E. F. Smith for separating uranium from the alkalies, the alkaline earths, and the rare earths in the analysis of certain rare minerals.

A very peculiar property of uranium is that it is not deposited as metal on the cathode, but as the hydrated protosesquioxide. Molybdenum is the only other metal known which, like uranium, is deposited as oxide on the cathode.

EXPERIMENTAL.

This research was made in order to fully confirm the reliability of the electrolytic method for the estimation of uranium and its

[1] *Am. Chem. J.*, **1**, 329 (1879); this Journal, **20**, 279 (1898).

separation from the alkalies, and also to find the conditions which are best suited for rather dilute solutions.

The cathodes for the first six experiments, when a current of $N.D_{140} = 0.6$ to 0.7 ampere was employed, were two platinum dishes of about 250 cc. capacity. For experiments Nos. 7 to 10, the cathode was a platinum dish of about 150 cc. capacity.

The anodes were made of heavy platinum wire. One was made of 30 cm. of No. 12 gauge platinum wire wound into a flat spiral of 4 cm. diameter. The other anode was made of 37 cm. of No. 14 gauge platinum wire wound into a flat spiral of 4 cm. diameter. The results obtained by the use of either anode were the same.

Storage cells were the source of current.

For the electrolysis, a measured amount of standard uranium nitrate solution was run into a cleaned and weighed platinum dish. A known amount of sodium acetate and of acetic acid was added, and the solution diluted to a definite volume. After heating to about 60° C., the current was started and the electrolyzation continued till the solution was clear and colorless, and no uranium was indicated when about 2 cc. of the electrolyte was removed and tested with potassium ferrocyanide in the presence of hydrochloric acid. As soon as all the uranium was precipitated, the current was interrupted and the electrolyte was emptied into a beaker. The black deposit was several times washed with warm distilled water. The electrolyte and washings were then poured through a fluted filter, so as to prevent the loss of any particles of the deposit which are apt to be removed during washing. The filter was washed with warm water, dried over a Bunsen flame, ignited, and added to the dish. The dish was ignited at "redness" for about fifteen minutes, after which it was allowed to cool in a desiccator. The dish was weighed and the final weight taken when it had remained on the balance pan for about five minutes, thus allowing its weight to become constant.

The deposit consisted principally of black hydrated protosesquioxide of uranium ($U_3O_4.3H_2O$), which on ignition changed to U_3O_8.

At the beginning of the electrolysis the deposit formed as yellow uranic hydroxide, but as the deposition continued it changed to the black hydrated protosesquioxide.

The results obtained[1] are :

Experiment No.	Grams of sodium acetate.	Amount of glacial acetic acid. cc.	Dilution. cc.	Current. N.D$_{140}$ = ampere.	Current. Volts.	Temperature. °C.	Time in hours.	Theoretical am't of U_3O_8 taken.	Weight of deposited U_3O_8.
1	2	0.7 Drops.	200	0.55	5	68–70	8	0.1098	0.1095
2	2	12 cc.	200	0.60	5	70	7	0.1098	0.1097
3	2	0.5	200	0.60–0.65	8–6	68–75	5	0.1098	0.1100
4	2	0.5	200	0.65	8–7.3	65–67	5½	0.1318	0.1319
5	2	0.5	200	0.65	7.5–6	68–70	5	0.1318	0.1318
6	2	0.5	200	0.60–0.65	8–5.5	69–71	5½	0.1318	0.1320

These results were obtained by electrolyzing a solution of 200 cc. volume with a current of N.D$_{140}$ = 0.55 to 0.65 ampere.

The results obtained, when a solution of 125 cc. was electrolyzed with a current of N.D$_{100}$ = 0.70 to 1.50 ampere, are as follows :

Experiment No.	Grams of sodium acetate.	Amount of 50 per cent. acetic acid. cc.	Dilution. cc.	Current. N.D$_{100}$ = amperes.	Temperature. °C.	Time in hours.	Theoretical a m't of U_3O_8 taken.	Weight of deposited U_3O_8.
7	1.0	2	125	0.70–0.85	80–85	6	0.1361	0.1363
8	2.0	2	125	0.70–0.93	70–80	6½	0.1814	0.1816
9	2.0	2	125	0.95–1.50	70–75	7½	0.2268	0.2270
10	0.3	1	125	0.90–1.30	73–80	8	0.2268	0.2260

According to the above results, the best conditions for the electrolytic precipitation of uranium from a rather dilute acetate solution are as follows: To the solution containing about 0.10 gram of U_3O_8 add from 1 to 2 grams of sodium acetate (if alkalies are present, no sodium acetate is needed) and from 1 to 2 cc. of 50 per cent. acetic acid, or if glacial acetic acid is used only half the quantity is needed. Dilute to from 125 to 200 cc., heat to about 65° C. and electrolyze with a current of N.D$_{140}$ = 0.60 to 0.70 ampere and 6 to 8 volts. The uranium is completely precipitated in from five to seven hours.

With solutions containing about 0.15 gram of U_3O_8 more current

[1] This part of the work, including experiments 1–6, was done under the direction of Prof. E. F. Smith at the University of Pennsylvania, during April, 1900.

is necessary, and the best conditions are: Add from 1 to 2 grams of sodium acetate, and from 1 to 2 cc. of 50 per cent. acetic acid, dilute the solution to 125 cc. and electrolyze with a current of $N.D_{100}$ = from 0.70 to 1.0 ampere. The temperature of the solution should be about 65° to 70° C. After the current is started no heat need be applied outwardly as the current itself keeps the solution heated. The time required for the complete precipitation of about 0.15 gram of U_3O_8 is from six and one-half to seven and one-half hours.

When solutions containing more than 0.15 gram of U_3O_8 were electrolyzed, some difficulty was experienced in precipitating all within eight hours by a current not exceeding $N.D_{100}$ = 1 ampere. With a current greater than this the deposits were very spongy and peeled from the dish; so the amount of U_3O_8 in solution should not exceed 0.15 gram.

The electrolytic precipitation of uranium has been used a number of times for the estimation of uranium and for separating it from the alkalies and alkaline earths. The results obtained were concordant with those obtained by precipitating it gravimetrically.

The simplicity of the electrolytic method for the determination of uranium, and the short time required, are in favor of this method.

SEPARATION OF URANIUM FROM PHOSPHORIC ACID.

Review of Methods.

Reynoso's Method.[1]—The uranium compound should be in solution as nitrate, having a small amount of free nitric acid present. Dilute to about 150 cc., add a strip of pure metallic tin, and boil. The phosphoric acid unites directly with the tin, to form oxyphosphate of tin, which is insoluble. The precipitate is filtered off and thoroughly washed. The filtrate is made alkaline with ammonia, and the precipitate which forms is treated with acetic acid. If it does not entirely dissolve, nitric acid is added and the precipitation by pure metallic tin repeated.[2] Heat the solution to boiling, filter off the oxyphosphate of tin, and wash with warm water. The precipitate rarely contains any uranium. The tin in the filtrate is removed by

[1] *Ann. Chem.* (Liebig), 81, 368 (1852).

[2] Fremy's "Encyclopédie Chimique," p. 86, (1884).

means of hydrogen sulphide. The filtrate from the tin sulphide is boiled till all hydrogen sulphide is expelled, after which the uranium is determined by any of the ordinary methods.

W. Hintz[1] had occasion to investigate this method and stated that a complete separation of phosphoric acid from uranium is effected by means of metallic tin.

Knopp and Arendt Method.[2]—The separation of uranium from phosphoric acid may be effected by fusing the ignited mass of uranium and phosphoric acid with a mixture of potassium cyanide and potassium carbonate, and treating the fused mass with warm water to dissolve out the phosphoric acid as soluble alkaline phosphate. The uranium is left as protoxide, which is reignited and weighed, or else dissolved in acid and precipitated by ammonia. The phosphoric acid in the filtrate is precipitated with magnesia mixture and weighed as magnesium pyrophosphate. Hintz[3] used sodium carbonate in place of potassium carbonate, and obtained very satisfactory results.

E. Reichardt's Method[4] is based on the direct precipitation of phosphoric acid, from an acetate solution as uranyl-ammonium phosphate, provided the uranium is in excess. The precipitate is filtered off, washed, dissolved in a solution of sodium carbonate, and the solution added to a solution of magnesia mixture, which precipitates the phosphoric acid as magnesium ammonium phosphate. If iron is present it is first precipitated from a nitric acid solution by adding an excess of sodium carbonate and boiling.[5] The phosphoric acid in the filtrate is precipitated as magnesium ammonium phosphate, and the uranium determined by the ordinary method, after expelling all the carbon dioxide.

Fresenius and Hintz Method.[6]—This method provides a means of separating arsenic and phosphoric acid from copper, uranium, and iron. Have the solution feebly acid with hydrochloric acid, add an excess of potassium ferrocyanide, then saturate with sodium chloride. The ferrocyanides of copper, uranium, and iron are washed by decantation, and subsequently decomposed by a warm solution of caustic potash, changing them to hydroxides.

[1] *Ann. Chem.* (Liebig), **151**, 216 (1869).
[2] *Chem. Centrbl.*, **773**, (1856).
[3] *Ann. Chem.* (Liebig), **151**, 216 (1869).
[4] *Ztschr. anal. Chem.*, **8**, 116 (1869); *Bull. Soc. Chim.*, **20**, 347 (1873).
[5] *Ztschr. anal. Chem.*, **8**, 116 (1869).
[6] *Ibid.*, **34**, 437; *Chem. News*, **72**, 206 (1895).

Filter and wash with a dilute solution of ammonium chloride till no ferrocyanide is recognized in the washings. The mixed hydroxides are treated with dilute hydrochloric acid. If any residue remains it is decomposed by a warm solution of caustic potash, going through with the same treatment as before. The solution by hydrochloric acid is free from arsenic and phosphoric acid. The copper, iron, and uranium are separated by ordinary methods.

Friedel and Cumenge[1] separated phosphoric acid from uranium by dissolving the substance in nitric acid, and precipitating the phosphoric acid with ammonium molybdate.

This method was used[2] for estimating the amount of phosphoric acid in precipitates of uranous phosphate, which were formed by electrolysis. The sample was dissolved in 30 cc. nitric acid (sp. gr. 1.42) and 3 cc. hydrochloric acid (sp. gr. 1.20). When iron was present, the sample was dissolved in a mixture of 20 cc. hydrochloric acid (sp. gr. 1.20) and 10 cc. nitric acid (sp. gr. 1.42). The solution was diluted to about 100 cc., and nearly neutralized with ammonia. A few drops of nitric acid were added to clear the solution, making it slightly acid, then to the hot solution (not above 65° C.) 50 cc. of molybdate solution[3] for every decigram of phosphorus pentoxide present. After digesting at 65° C. for an hour and a half, the yellow precipitate was filtered, and washed with cold water. The filtrate was tested for phosphoric acid by adding more molybdate solution and reheating at 65° C. The yellow precipitate of ammonium phosphomolybdate was dissolved from the filter with ammonia and hot water, and washed into a beaker to a bulk not exceeding 100 cc. It was nearly neutralized with hydrochloric acid, cooled, and magnesia mixture added, drop by drop from a burette, stirring all the while. After about twenty minutes, 30 cc. ammonia (sp. gr. 0.96) were added and the solution allowed to stand in the cold for three hours. The precipitate of magnesium ammonium phosphate was filtered and washed with dilute ammonia (2.5 cc. ammonia and 100 cc. water) till free from chlorides. The precipitate was dried, ignited, and weighed as magnesium pyrophosphate.

The uranium in the filtrate, from the ammonium phospho-

[1] *Am. J. Sci.*, **10**, 135 (1900).

[2] At the University of Pennsylvania in 1900.

[3] Prepared according to the formulas given in the "Official Methods of the U. S. Agricultural Chemists.

molybdate, was determined by three precipitations with ammonia, and weighed as U_3O_8.

PART II.—THE DETERMINATION OF URANIUM.

DETERMINATION OF URANIUM AS OXIDE.

The precipitant which Péligot used in 1840 for the estimation of uranium was ammonia, the principal reagent used for that purpose at the present time. The yellow precipitate which forms when ammonia is added to a uranyl solution is hydrated ammonium uranate[1] ($(NH_4)_2U_2O_7.xH_2O$, or $(NH_4)_2O.2UO_3.xH_2O$), which is soluble in alkali carbonate solutions, and slightly soluble in pure water; but in water containing ammonia, ammonium nitrate, or ammonium chloride it is insoluble.[2] The presence of tartaric acid, oxalic acid, or non-volatile organic substances prevents the precipitation of ammonium uranate.[3]

If the solution contains any alkalies or alkaline earths, a portion of these will be precipitated along with the uranium.[4]

Berthier's Method.[5]—The reagent next in importance to ammonia, for the estimation of uranium, is ammonium sulphide, which was first used (in 1840) by Berthier. A complete precipitation of uranium by ammonium sulphide is obtained, provided the solution is previously nearly neutralized by ammonia, and no carbonates are present. The precipitate which forms is usually black in color, sometimes changing to reddish brown.[6] When a large excess of the precipitant is added and it is allowed to stand, the liquid sometimes assumes a brown color.[7] This color, says Zimmerman,[8] is due to the solubility of uranyl sulphide in ammonium carbonate contained in the ammonium sulphide. When the ammonium sulphide contains a considerable amount of thiosulphate the red sulphide described by Remele[9] is formed; but when thiosulphate is absent only the dark precipitate results. Thiosulphate in the reagent is due to the oxidation of ammonium sulphide by atmospheric oxygen.

In 1865, A. Remele studied the method for the estimation of

[1] *Chemiker Kalender*, p. 270, (1899).
[2] Comey's "Dictionary of Chemical Solubilities."
[3] Fresenius' "Qualitative Chemical Analysis," 219.
[4] *Ibid.*, 6th edition, p. 533.
[5] *Ann. Chem.* (Liebig), **46**, 184.
[6] Pogg. *Ann.*, **116**, 352.
[7] *Ibid.*, **124**, 120.
[8] *Ann. Chem.* (Liebig), **204**, 224 (1880).
[9] Pogg. *Ann.*, **116**, 352.

uranium by the use of ammonium sulphide and found the best results were obtained by the following procedure:[1] The ammonium sulphide should be fresh and kept well corked, as it absorbs carbon dioxide when exposed to the atmosphere. To the nearly neutral ammoniacal solution, add an excess of yellow ammonium sulphide and keep the solution near boiling for an hour, in order to convert the $(UO_2)S$, which is first formed, into a mixture of UO_3 and sulphur. This precipitate is rapidly dissolved by alkali carbonates and by tartaric acid. It is slightly soluble in pure water, is soluble in dilute, but insoluble in absolute, alcohol. It is readily soluble in acids, even acetic acid.[2] The presence of ammonium chloride or ammonium nitrate assists the precipitation of $(UO_2)S$, as it is less soluble in these solutions. The precipitate, containing all the uranium, is filtered off and washed with cold or hot water containing a small amount of ammonium sulphide and ammonium chloride or nitrate. Wash first by decantation and finally on the filter. The precipitate during washing passes to yellow uranic hydroxide. It is dried, then roasted to remove all the sulphur and finally converted into U_3O_8 by ignition in the air, or into UO_2 by ignition in a current of hydrogen and allowing to cool in same.

A complete separation of uranium from the alkalies and alkaline earths is obtained by means of ammonium sulphide.[3]

C. Winkler made a comparison of this method with Péligot's ammonium method[4] and states that the precipitation of uranium by pure ammonium sulphide is trustworthy.[5]

EXPERIMENTAL.

Precipitation of Uranium by Ammonia.—For each determination a measured amount of standard uranium nitrate solution was run into a beaker and enough distilled water added to bring the volume to from 150 to 200 cc. The solutions were brought to boiling and a few drops of nitric acid added, and the uranium precipitated by adding an excess of ammonia to the hot solution. The precipitates which formed were a bright lemon-yellow color and settled rapidly. The precipitates were allowed to settle, and washed several times by decantation and twice on the filter with

[1] *Ztschr. anal. Chem.*, **4**, 379.
[2] Comey's "Dictionary of Chemical Solubilities," 1896.
[3] *Ztschr. anal. Chem.*, **1**, 411.
[4] Fresenius' "Quantitative Chemical Analysis," p. 281.
[5] *Chem. News*, **43**, 153 (1881).

warm dilute ammonium chloride solution (2 grams salt to 100 cc. water), after which they were dried in a hot oven, and ignited and weighed as oxides.

The following table gives the conditions observed:

THE THEORETICAL AMOUNT OF URANIUM TAKEN WAS 0.1925 GRAM.

Experiment No.	Approximate dilution. cc.	Salts present.	Crucible in which ignited.	Weighed as:	Weight of U_3O_8.	Uranium equivalent of U_3O_8.	Ignited in hydrogen for: Hours.	Weight of UO_2.	Uranium equivalent of UO_2.
1	200	NH_4Cl	Platinum	U_3O_8	0.2242	0.19130	..	....	.....
2	200	NH_4Cl	Platinum	U_3O_8	0.2268	0.19252	..	....	.....
3	150	NH_4Cl	Platinum	U_3O_8	0.2269	0.19260	..	....	.....
4	150	NH_4Cl	Platinum	U_3O_8	0.2266	0.19235	..	....	.....
5	175	NH_4Cl	Platinum	U_3O_8	0.2268	0.19252	2	0.2191	0.19329
6	175	NH_4Cl + $CHCl_3$	Platinum	U_3O_8 + UO_2	0.2267	0.19243	$\frac{3}{4}$	0.2179	0.19223
7	175	NH_4Cl + $CHCl_3$	Porcelain	U_3O_8	0.2269	0.19260	$2\frac{1}{2}$	0.2207	0.19479
8	150	NH_4Cl	Platinum	U_3O_8	0.2268	0.19252	1	0.2211	0.19505
9	150	NH_4Cl	Platinum	U_3O_8	0.2270	0.19268	$\frac{3}{4}$	0.2221	0.19593
10	150	NH_4Cl + Alcohol	Porcelain	U_3O_8	0.2280	0.19353	..	....	.....
11	175	NH_4Cl + Alcohol	Porcelain	U_3O_8	0.2270	0.19268	..	....	.....
12	175	NH_4Cl	Platinum	UO_2	....	.....	$\frac{1}{2}$	0.2180	0.19232
13	150	NH_4Cl	Porcelain	....	....	.....	1	0.2240	0.19761

U_3O_8 multiplied by 0.84884 gives the uranium equivalent; UO_2 multiplied by 0.88218 gives the same. These are the factors obtained by taking the atomic weight of uranium as 239.6 and that of oxygen as 16.[1]

For all the above precipitations the solutions, of from 150 to 200 cc. volume, were made decidedly acid with from 0.5 to 1 cc. nitric acid (sp. gr. 1.42), brought to boiling and ammonia added in excess. Some of the solutions were boiled for about fifteen minutes after the precipitation by ammonia, while others were filtered directly without boiling. The boiling caused the lemon-yellow colored voluminous amorphous precipitate to change to a more crystalline form, less voluminous and of a slightly darker color. The precipitates which were boiled were much easier to filter and wash, and were less liable to pass through, which usually happened when boiling was omitted.

[1] This Journal, **23**, 94 (1901).

The presence of chloroform or alcohol (as recommended by some chemists) did not assist the precipitation, but the presence of ammonium chloride or ammonium nitrate was essential. Five to ten grams were added previous to the addition of ammonia.

Some of the precipitates were ignited separate from the paper, and others without separating from the paper. The results obtained, whether the precipitates were ignited separately or not, were identical, showing that it is unnecessary to ignite the precipitate and the filter-paper separately, as is recommended by the German chemists.

When the uranium was weighed as U_3O_8, the precipitates together with the filter-paper were placed in a crucible and slowly ignited till the paper had completely burned; then the ignition was continued for about fifteen minutes in a blast-flame, and allowed to cool slowly in a gradually decreasing Bunsen flame. During ignition the crucibles were placed in a slanting position in order to allow of free circulation of air in the crucible, thus obtaining complete oxidation. The results were the same whether porcelain or platinum crucibles were used.

In all directions given in text-books and journals for weighing uranium as oxide, it is recommended that the dry precipitate of ammonium uranate be strongly ignited over a blast-lamp to U_3O_8, and allowed to slowly cool in a gradually decreasing flame and finally in a desiccator. It is then weighed, and as a means of ascertaining its purity for the purpose of control, it is reignited in a current of pure hydrogen and reduced to its lower oxide, UO_2. This was tried, but only in one case was it possible to completely reduce U_3O_8 to UO_2, even when the ignition in hydrogen was continued for two hours. This time (experiment No. 6) the reduction was brought about by using a platinum crucible and igniting strongly in a current of pure hydrogen over the hottest blast-lamp that could be obtained. When a porcelain crucible was used in which the ignition was made, the reduction did not proceed so far as when a platinum crucible was used. The reason for this is the fact stated by Roberts-Austen[1] as follows: "Saint Claire Deville and Troost discovered that hydrogen and hydrocarbons pass through platinum at a red heat." The further reduction of U_3O_8, when a platinum crucible is used, would seem to indicate that hydrocarbons of the flame play as important a

[1] Roberts-Austen's "Introduction to Metallurgy," p. 54, (1898).

part in the reduction as the hydrogen. It was impossible to obtain a single complete reduction of the precipitate to UO_2 when a porcelain crucible was used, even when the precipitate was not previously ignited. When a platinum crucible was used, and the precipitate not previously ignited in the air, the complete reduction to UO_2 occurred within half an hour by igniting it in a current of pure hydrogen over a blast-lamp, and allowing it to cool in an atmosphere of hydrogen over a gradually decreasing flame. The U_3O_8 is a velvety black colored mass, and the UO_2 a dull brown colored mass.

For the above reductions ordinary porcelain and platinum Rose crucibles were used. The hydrogen was purified by Schobig's method,[1] by first passing it through a strong solution of potassium permanganate to remove the hydrides of arsenic, antimony, phosphorus, and carbon; then through a strong solution of caustic soda to remove hydrogen sulphide; and finally through sulphuric acid (sp. gr. 1.84) to remove moisture.

DETERMINATION OF URANIUM AS PHOSPHATE.

Review of Method.

The precipitation of uranium by an alkali phosphate has rarely been employed as a means of estimating uranium, because the precipitate which forms is gelatinous and difficult to wash free from alkali. This trouble has been overcome by adapting the method to volumetric means, which is the reverse of the volumetric estimation of phosphoric acid by a standard uranium solution. The uranium in solution as acetate is titrated by means of a standard solution of sodium-hydrogen-ammonium phosphate ($NaHNH_4PO_4$), which is added till a drop of the precipitated solution brought in contact with a drop of freshly prepared solution of potassium ferrocyanide does not give a brown coloration.[2]

The quantitative estimation of uranium by means of an alkali phosphate was first suggested by Leconte[3] and later worked out by Pisani;[4] but owing to the difficulty of filtering and washing the greenish yellow, slimy precipitate of UO_2HPO_4, this method has not come into use.

[1] *J. prakt. Chem.*, (2), **14**, 289–299.

[2] Mohr's "Lehrbuch der Chemisch-analytischen Titrirmethode," p. 521. Dammer's "Handbuch der anorg. Chemie," **3**, 686 (1893).

[3] Liebig and Kopp: *Jahresbericht*, p. 642, (1853).

[4] *Chem. News*, **3**, 211 (1862).

EXPERIMENTAL.

Were it not for the difficulty of washing the uranium phosphate, which is formed by disodium hydrogen phosphate, this method would afford a decided advantage over precipitating it with ammonia and weighing it as oxide (U_3O_8) because any error would be greatly diminished by weighing as $(UO_2)_2P_2O_7$. U_3O_8 multiplied by 0.84884 gives the uranium equivalent, while $(UO_2)_2P_2O_7$ multiplied by 0.66815 gives the same; so by weighing the uranium as pyrophosphate the error or loss is decreased.

This method was studied, and the best conditions for weighing uranium as uranyl pyrophosphate were worked out, the results of which are tabulated below.

PRECIPITATION OF URANIUM BY DISODIUM HYDROGEN PHOSPHATE.

Experiment No.	Approximate dilution. cc.	Salts added.	Temperature of solution after precipitation.	Crucible in which ignited.	Time of ignition. Minutes.	Weight of $(UO_2)_2P_2O_7$	Uranium equivalent.	Theoretical amt of uranium taken.
1	150	NH_4NO_3 + $NN_4C_2H_3O_2$	Cold, then heated to b.p.	Platinum	15	0.2875	0.1921	0.1925
2	150	NH_4Cl + $NH_4C_2H_3O_2$	"	"	10	0.2884	0.1927	0.1925
3	150	NH_4NO_3 + $NH_4C_2H_3O_2$	"	Porcelain	10	0.2878	0.1923	0.1925
4	150	NH_4NO_3 + $NH_4C_2H_3O_2$	b.p. for 1 hour after precipit.	Platinum	10	0.2851	0.1905	0.1925
5	150	Chloroform + $NH_4C_2H_3O_2$	"	"	10	0.2848	0.1903	0.1925
6	150	NH_4NO_3 + $NH_4C_2H_3O_2$	"	Porcelain	15	0.2875	0.1921	0.1925
7	150	Chloroform + $NH_4C_2H_3O_2$	"	"	20	0.2870	0.1918	0.1925

These determinations were made by measuring 50 cc. of standard uranium nitrate solution into a beaker, diluting to 150 cc. and adding nitric acid (sp. gr. 1.42), varying the amount from 0.5 cc. to 1.5 cc. The solutions were brought to boiling and ammonia (sp. gr. 0.90) added to neutral reaction and a measured amount in excess—from 1 cc. to 10 cc. The yellow precipitate of ammonium uranate was dissolved by adding 50 per cent. acetic acid till the precipitate disappeared, and then an excess varying from 1 cc. to 5 cc. To the solution—which contained besides uranium acetate, an excess of acetic acid, ammonium nitrate, and

ammonium acetate—an excess of a saturated solution of disodium hydrogen phosphate was added. The precipitate which formed was greenish white in color and voluminous. The solution was brought to boiling, then allowed to cool, and filtered. In experiments Nos. 4 to 7 the solutions were kept for one hour on water-baths at the temperature of boiling water, after which they were allowed to cool, then filtered. This treatment assisted the settling of the precipitate, but did not change its gelatinous character.

The washing of the precipitates was done by four decantations and twice on the filter with a hot dilute solution of ammonium chloride (2.5 grams of salt to 100 cc. of water). The washing was not so easy as the ammonium uranate precipitates, even when as much as 5 grams of ammonium chloride were added to the solution previous to its precipitation. Neither the addition of chloroform nor of ammonium chloride had any effect on the appearance of the precipitate, as there were already sufficient ammonium salts present, formed by the neutralization of nitric acid by ammonia and of ammonia by acetic acid.

The precipitates, after washing, were dried at a temperature of from 100° C. to 115° C., separated from the filter-paper, which was first ignited in the crucible, then the precipitate added and the ignition continued for from ten to twenty minutes at "redness" over a Bunsen burner. The residue in most cases was green in color, due to the partial reduction of uranyl pyrophosphate. Whenever the temperature of ignition was above "redness" a reduction always occurred, especially when a platinum crucible was used. When a porcelain crucible was used the ignition could be done at "redness," but above this temperature (as over a blast-lamp) reduction always resulted.

The reduced uranyl pyrophosphate was not weighed as such, but was moistened with a few drops of nitric acid (sp. gr. 1.42), dried over a low flame, and reignited at "low redness" over a Bunsen burner. The mass after such treatment was always of a lemon-yellow color. The weight of the yellow uranyl pyrophosphate remained constant, no matter how long it was ignited at a temperature not exceeding "low redness," but above this temperature it always lost weight and assumed a green color. Whenever this occurs it may be reoxidized by treating it with nitric acid and reigniting at "low redness."

This green residue of pyrophosphate most probably has the composition $U_2O_3.P_2O_7$, which is indicated by the weights of several which varied from 0.2820 to 0.2827 gram. 0.2820 multiplied by 0.6833 gives 0.1929 gram uranium, the theoretical amount of uranium being 0.1925 gram.

One of the residues which was more intensely ignited than the others, with the cover on the platinum crucible, was of a reddish brown color. Its weight was 0.2800 gram, showing that the reduction had gone further than $U_2O_3.P_2O_7$.

The composition of the lemon-yellow colored uranyl pyrophosphate is $(UO_2)_2P_2O_7$.

PRECIPITATION OF URANIUM BY AMMONIUM DIHYDROGEN PHOSPHATE.

As the precipitates formed by disodium hydrogen phosphate were slimy and difficult to wash, it was suggested that possibly this difficulty could be overcome by means of an ammonium phosphate. The precipitant used was ammonium dihydrogen phosphate. The mode of procedure was the same as when disodium hydrogen phosphate was used.

To a solution containing 0.1925 gram of uranium were added from 0.1 cc. to 1.5 cc. nitric acid (sp. gr. 1.42) and sufficient water to make 150 cc. volume. The solution was brought to boiling, ammonia (sp. gr. 0.90) was added to neutral reaction and from 1 cc. to 10 cc. in excess. The ammonium uranate which formed was taken into solution by the addition of 50 per cent. acetic acid and from 1 cc. to 5 cc. in excess. The solutions, then acid with acetic acid, were brought to boiling and the uranium precipitated by an excess of a saturated solution of ammonium dihydrogen phosphate. The best precipitations, that is, those which were most crystalline and easiest to handle, were formed when about one and a half as much precipitant was added as was necessary for the precipitation. The solutions were boiled for half an hour, and the precipitate allowed to settle before filtering. The precipitates were washed three times by decantation and three times on the filter with a hot dilute solution of ammonium chloride (2 grams salt to 100 cc. water). The addition of ammonium chloride or of chloroform to the solution was found unnecessary, as enough ammonium salts were already present. The precipitates which formed were pulverulent and crystalline,

and were as readily filtered and washed as the precipitates of ammonium uranate.

The precipitates were dried, separated from the filter-paper, and the paper ignited in a porcelain crucible, after which the precipitate was added and the ignition continued at "redness" for about five minutes. The crucible was allowed to cool and the residue moistened with a few drops of nitric acid (sp. gr. 1.42). The mass was dried over a low flame, then reignited for from ten to twenty-five minutes at "low redness" over a Bunsen burner. The mass after this treatment was, in all cases, a lemon-yellow color. The crucibles were allowed to cool in a desiccator, and weighed.

The results obtained are as follows:

PRECIPITATION OF URANIUM BY AMMONIUM DIHYDROGEN PHOSPHATE.

Experiment No.	Approximate dilution. cc.	Salts added.	Temperature of solution after precipitation.	Crucible in which ignited.	Time of ignition. Minutes.	Weight of $(UO_2)_2P_2O_7$.	Uranium equivalent.	Theoretical amount of uranium taken.
8	150	NH_4NO_3, $NH_4C_2H_3O_2$	b.p., boiled for 1 hour.	Porcelain	10	0.2879	0.1924	0.1925
9	150	"	b.p., boiled for 10 min.	"	15	0.2880	0.1924	0.1925
10	200	"	b.p., boiled for $\frac{3}{4}$ hour.	"	20	0.2881	0.1925	0.1925
11	200	"	"	"	20	0.2879	0.1924	0.1925
12	150	NH_4Cl, NH_4NO_3, $NH_4C_2H_3O_2$	"	"	25	0.2881	0.1925	0.1925
13	150	NH_4NO_3, $NH_4C_2H_3O_2$	"	"	25	0.2883	0.1926	0.1925
14	200	"	"	"	15	0.2879	0.1924	0.1925
15	150	NH_4Cl, $NH_4C_2H_3O_2$	"	"	15	0.2878	0.1923	0.1925
16	150	"	"	"	15	0.2882	0.1926	0.1925

The filtrates were evaporated and tested for uranium with potassium ferrocyanide. No uranium was indicated.

In several cases when the ignition was done at a temperature above "redness," the precipitate would invariably assume a green color, especially where the residue was in contact with the crucible. Whenever this occurred, the mass was again moistened with nitric acid (sp. gr. 1.42), dried over a low flame, and reignited at "low redness." By this treatment the mass was oxidized to $(UO_2)_2P_2O_7$.

Several precipitates, after having been weighed as uranyl pyrophosphate, were reignited over a blast-lamp for about fifteen minutes. The residue, in all cases, after such treatment was entirely green, but when moistened with nitric acid (sp. gr. 1.42) and reignited at "low redness," always changed back to lemon-yellow uranyl pyrophosphate, and their weight was the same as the original weight.

Solution No. 15 was allowed to stand for six days before filtering. The appearance of the precipitate was the same as those which were filtered directly.

The weighing of uranium as uranyl ammonium phosphate ($UO_2.NH_4.PO_4$) was undertaken, but without success. The filtering through Gooch crucibles was tried, but owing to the fineness of the precipitate this could not be done. After trying to filter six solutions in this manner, the idea of weighing uranium as uranyl ammonium phosphate was abandoned as impracticable.

THE VOLUMETRIC ESTIMATION OF URANIUM.

Belohoubeck,[1] in 1866, estimated uranium by reducing the solution in a flask with metallic zinc and sulphuric acid. For small amounts of uranium, he states that the reduction is complete in about fifteen minutes, while for larger quantities the time required is much longer. The solutions, after reduction, were diluted and titrated by a standard potassium permanganate solution, the standard of which was made on ferrous ammonium sulphate.

Uranium differs from iron, as regards reduction, in that it is not reduced by hydrogen sulphide. When mercuric salts are present the uranium is, however, reduced by this reagent.[2]

The permanganate used for titrating uranium solutions is standardized by iron, two atoms of iron corresponding to one of uranium.

The reaction[3] which occurs during the titration of sulphate solutions of uranium is:

$$5U(SO_4)_2 + 2KMnO_4 + 2H_2SO_4 + 2H_2O = 5(UO_2)SO_4 + 2MnSO_4 + 2KHSO_4 + 3H_2SO_4.$$

The reaction which occurs during the titration of ferrous solution is:

[1] *Zischr. anal. Chem.*, **6**, 120 (1867); Sutton's "Volumetric Analysis," p. 375, (1900).
[2] Dammer's "Handbuch der anorg. Chemie," Vol. III, p. 686 (1893).
[3] Mohr's "Lehrbuch der chem.-analyt. Titrirmethoden," p. 267.

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

$5U(SO_4)_2$ is equivalent to $10FeSO_4$, or $1U = 2Fe$.

The reduction of uranium by zinc and sulphuric acid corresponds to the change of UO_3 to UO_2.[1]

EXPERIMENTAL.

The fact that iron is so easily and, at the same time, accurately determined by means of potassium permanganate, and that uranium solutions can be reduced, and then oxidized by potassium permanganate, suggested that possibly, with a few modifications, the Belohoubeck method could be adapted to the technical assay of uranium ores.

In order to demonstrate the best means of reducing uranium solutions, several different reducing agents were employed, the results of which are given below:

The first series of experiments was made by reducing the uranyl solution by means of zinc and sulphuric acid at boiling temperature, then by means of zinc and hydrochloric acid.

The second series was made by reducing the uranyl solution by means of strips of metallic aluminum, first in dilute sulphuric acid solutions, then in dilute hydrochloric acid solutions.

The third series was made by reducing the uranyl solutions by means of metallic magnesium, first in dilute sulphuric acid, then in dilute hydrochloric acid solutions.

The fourth series was made by passing the uranyl solutions through a long Jones' reductor.

The fifth series was made by reducing the uranyl solution by means of a strong solution of stannous chloride and destroying the excess of stannous chloride by adding sufficient mercuric chloride, as in the Zimmerman-Reinhart method, so largely used for the estimation of iron.

The standard solution of potassium permanganate was made by dissolving 18.96 grams of the salt in distilled water and diluting it to 6 liters, thus making a 0.01 normal solution. The standard was obtained by titrating ferrous sulphate solutions, containing a known quantity of iron.

$$1 \text{ cc. } KMnO_4 = 0.00548 \text{ gram iron.}$$

[1] Watts' "Chemical Dictionary," 4, 820.

The uranium standard was calculated from the iron standard by the proportion:

$$239.6 : 2\,(55.9) = x : 0.00548\,;\quad x = 0.01176.$$

Two equivalents of iron correspond to one equivalent of uranium, or the iron standard multiplied by 2.1425 gives the uranium standard. In order to get the uranium standard in terms of U_3O_8, multiply the iron standard by 2.5243.

The standard of the permanganate solution was verified by taking a measured amount of standard uranium nitrate solution, and reducing it with about 50 grams of pure zinc and sulphuric acid (30 cc. sulphuric acid (sp. gr. 1.84) in 150 cc. of solution). The solution was diluted to 500 cc. and titrated. The results obtained agreed to the fifth decimal place with those of the iron titration.

TITRATION OF URANIUM SOLUTIONS WITH POTASSIUM PERMANGANATE.

Zimmerman[1] recommends, when uranous solutions are titrated with standard potassium permanganate solution, that the permanganate be added in excess and the excess then titrated back with a standard solution of ferrous sulphate. He stated that by this procedure the oxidation of the uranous solution by air is prevented. In the following titrations—about sixty in number, and also a number of others made later—the recommendation of Zimmerman was not observed, but the uranous solution was titrated in the same manner as a ferrous solution. The oxidation of the uranous solutions was prevented by placing about 1 gram of dry sodium carbonate in the large Erlenmeyer flask in which the titrations were made. The mouth of the flask was closed by a 2½ inch funnel, and the solution which was reduced in a small Erlenmeyer flask was emptied into it. The solutions, which were quite acid, on coming in contact with the dry sodium carbonate, liberated carbon dioxide which filled the "titration flask" and prevented the oxidation of the uranous solutions.

The reductions, whether made by metallic zinc, aluminum, or magnesium, were made in a small 250 cc. Erlenmeyer flask, the mouth of which was closed by a small funnel. The uranyl solutions were poured into the flask, acidified, the metal added, and the reduction carried on at boiling temperature. After the reduc-

[1] *Ann. Chem.* (Liebig), **213**, 300 (1882).

tion had occurred, the funnel and sides of the flask were washed down with distilled water and the hot solution rapidly emptied into the "titration flask" which contained about 1 gram of dry sodium carbonate. The flask in which the reduction was made was rinsed out four times with cold distilled water, the rinsings poured into the "titration flask," and the solution diluted to from 500 to 600 cc. The titrations were made at once, adding the permanganate solution till pink "end-point," which was very delicate, when sulphate solutions were titrated.

The determinations were made as follows: A measured amount of standard uranium nitrate solution was measured into a small beaker, and from 10 to 15 cc. of sulphuric acid (sp. gr. 1.84), added. The solution was evaporated to dense white fumes, allowed to cool, then poured into an Erlenmeyer flask, which contained a small amount of water. The solution was diluted to a definite volume (100 to 200 cc.) and more sulphuric acid added.

The best and most rapid reductions occurred when the amount of free sulphuric acid (sp. gr. 1.84) present was within the limits, 1 part acid to 4 parts solution, and 1 part acid to 5 parts solution. When the concentration is more than 1 to 4, the metal, especially zinc, is coated with a rather insoluble sulphate which retards the generation of hydrogen.

Comparing the time required for the complete reduction of uranyl solutions with that required for the reduction of iron solutions, it was found to be about twice as long, when equivalent amounts of uranium and iron salts were reduced.

When zinc was the metal used for generating the hydrogen, about 50 grams of pure metal (15 lumps) were used.

When the solutions were reduced by means of aluminum, fifteen strips of the metal were used, size 8 mm. wide by 15 mm. long, and 0.5 mm. thick.

The reductions by means of metallic magnesium were made by using eight pieces of a bar 8 mm. in diameter and 15 mm. long.

The reductions, whether made by means of metallic zinc, aluminum, or magnesium, were in all cases the same. The only difference noticed was the rapidity of solution of the metals; aluminum dissolved more rapidly than zinc, and magnesium more rapidly than aluminum. The reduction, whether carried on at boiling temperature for one hour, or for as long as five hours, did not go further than $U(SO_4)_2$. The time required for the reduc-

tion of about 0.1 gram of uranium by zinc is about one hour, for about 0.2 gram not less than one and a half hours. The uranyl sulphate solution, at first yellow in color, changes to light green and finally to green with bluish tinge, having the appearance of a dilute solution of nickel chloride, which color it retains even though the reduction be continued for as long as four hours.

The results, which were obtained by titrating uranous sulphate solutions, are all that can be desired, as they agree within analytical limits with those obtained by the standard gravimetric method, which is to precipitate the uranium with ammonia, and weigh it as U_3O_8.

The reduction of hydrochloric acid solutions was also tried. For this purpose, a measured amount of standard uranium nitrate solution was twice evaporated to dryness with 10 cc. hydrochloric acid (sp. gr. 1.20). The dry mass of uranyl chloride was taken up with 15 cc. hydrochloric acid (sp. gr. 1.20), and water added, after which the solution was poured into a small Erlenmeyer flask and diluted to from 100 to 200 cc. More hydrochloric acid was added, and the solutions reduced at boiling temperature in the same manner as the sulphate solutions. The reductions were made first by the use of metallic zinc, then by metallic aluminum, and lastly by metallic magnesium. In all cases when the reduction was carried on for from two to four hours, it approached (and in several cases reached) the subchloride (U_2Cl_6 or UCl_3). With solutions of about 100 cc. volume and rather strongly acid (1 part hydrochloric acid (sp. gr. 1.20) to 4 parts solution), at boiling temperature the reduction to UCl_3 was complete within about two hours. By longer treatment the reduction went no further. The color of the hydrochloric acid solution of uranium, at first yellow, changed to green, to bluish green, to olive-green, and finally to reddish-brown —resembling the color of old port wine. The solutions, previous to titration, were cooled by running water, diluted to about 600 cc., and titrated in the same manner as the uranous sulphate solutions.

The "end-point" was not so delicate as when sulphate solutions were titrated. As no "preventative solution" was added, a small amount of chlorine was evolved after the solutions were allowed to remain standing for a few minutes. The interference of the "end-point" by chlorine was prevented by having a very small amount of free hydrochloric acid present, not over 3 per cent. of the total solution.

The results obtained are as follows:

REDUCTION OF URANYL SOLUTIONS BY METALLIC ZINC.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Hours.	Dilution at the time of titration. cc.	Amount of free acid present. cc.		Amount of $KMnO_4$ required. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
1	100	2¾	600	15	H_2SO_4	13.10	0.15406	0.15400
2	200	3	600	20	"	13.15	0.15464	0.15400
3	125	1¼	500	20	"	8.20	0.09643	0.09625
4	135	1¼	500	25	"	8.20	0.09643	0.09625
5	130	1	600	20	"	16.40	0.19286	0.19250
6	130	1	600	20	"	16.35	0.19228	0.19250
7	125	1¼	500	20	"	19.60	0.23050	0.23100
8	125	1½	500	25	"	19.65	0.23108	0.23100
9	100	2½	600	30	HCl	21.10	....	0.15400
10	200	2¾	600	25	"	19.80	....	0.15400

REDUCTION OF URANYL SOLUTIONS BY METALLIC ALUMINUM.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Hours.	Dilution at the time of titration. cc.	Amount of free acid present. cc.		Amount of $KMnO_4$ required. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
11	110	½	600	15	H_2SO_4	13.15	0.15464	0.1540
12	150	1½	600	20	"	13.05	0.15350	0.1540
13	150	2½	600	20	"	13.10	0.15406	0.1540
14	100	2¾	500	15	"	13.05	0.15350	0.1540
15	100	3	500	15	"	13.10	0.15406	0.1540
16	200	4	600	25	"	13.15	0.15464	0.1540
17	120	1½	600	30	"	13.15	0.15464	0.1540
18	200	2½	600	40	"	13.10	0.15406	0.1540
19	200	2½	600	50	"	13.15	0.15464	0.1540
20	75	1½	700	20	HCl	20.10	....	0.1540
21	75	1½	700	20	"	18.85	....	0.1540
22	200	3	700	20	"	17.40	....	0.1540
23	200	3	700	20	"	19.60	....	0.1540

REDUCTION OF URANYL SOLUTIONS BY METALLIC MAGNESIUM.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Hours.	Dilution at the time of titration. cc.	Amount of free acid present. cc.		Amount of $KMnO_4$ required. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
24	125	1	600	20	H_2SO_4	13.10	0.15406	0.1540
25	125	1	600	29	"	13.05	0.15347	0.1540
26	125	2¼	700	20	HC6	16.90	....	0.1540
27	125	2¼	700	20	"	17.60	....	0.1540

The reduction of uranyl solutions to the uranous state can also be made by passing the solution through a Jones reductor. The reductor used was much longer than those ordinarily employed for the reduction of iron solutions. It was made of a 50 cc. burette, in the lower part of which was placed an inch layer of broken glass and on top of this was poured an 18 inch column of 20 mesh amalgamated zinc. The amalgamation was done by washing the zinc with a warm dilute solution of mercurous nitrate, then thoroughly washing it with warm distilled water.

The determinations were made by taking a measured amount of standard uranium nitrate solution and evaporating it to dense white fumes with 10 cc. sulphuric acid (sp. gr. 1.84). The solution was allowed to cool, then diluted to from 100 to 150 cc. and more sulphuric acid added. The warm solution was poured through the reductor, and caught in a large Erlenmeyer flask which contained about 1 gram of dry sodium carbonate, and the mouth of which was closed by a small funnel. After all the solution had been emptied into the reductor, it was followed by about 250 cc. distilled water. The solution was then diluted to 500 cc., and titrated with 0.01 normal potassium permanganate solution to faint red end-reaction.

The time required for 100 cc. of uranyl solution and 250 cc. of water to pass through the reductor was about ten minutes; for 150 cc. uranyl solution and 250 cc. of water to pass through it required about twenty minutes.

Sutton[1] states that while washing the reductor free from iron solutions, the wash-water should be kept above the zinc level, so as not to allow of any air-spaces between the successive additions of water, in which case hydrogen peroxide is formed, thus causing high results. This caution was observed in the reductions.

The most satisfactory results were obtained when the ratio of free sulphuric acid (sp. gr. 1.84) to total solution was not less than 1 to 6, nor more than 1 to 5. When the solutions contained more acid than the ratio of 1 to 5, the zinc sulphate which formed did not go into solution, and prevented the ready passage of the solution through the reductor. When the acid was present in amounts less than the ratio of 1 to 7, the reduction of the solution was incomplete, due to too slow action of the acid on the zinc. The reduction was complete in all cases when the ratio of

[1] Sutton's "Volumetric Analysis," under "Iron."

free sulphuric acid (sp. gr. 1.84) to total solution was within the limits of 1 to 6 and 1 to 5. Even when the solutions were twice run through the reductor no further reduction occurred than when run through once.

The results obtained are shown in the table.

REDUCTION OF URANYL SOLUTIONS BY PASSING THROUGH REDUCTOR.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Minutes.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of $KMnO_4$ required. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
28	100	9	600	20 H_2SO_4	8.20	0.09643	0.09625
29	100	9	600	15 "	8.20	0.09643	0.09625
30	110	10	500	10 "	13.15	0.15464	0.1540
31	110	10	500	10 "	13.05	0.15347	0.1540
32	115	11	500	15 "	13.10	0.15406	0.1540
33	115	11	500	15 "	13.10	0.15406	0.1540
34	120	12	500	20 "	13.10	0.15406	0.1540
35	120	12	600	20 "	13.10	0.15406	0.1540
36	100	10	500	20 "	16.40	0.19286	0.1925
37	100	10	600	20 "	16.35	0.19228	0.1925
38	125	12	600	25 "	26.20	0.30810	0.3080
39	130	14	600	30 "	26.20	0.30810	0.3080
40	150	18	600	35 "	26.20	0.30810	0.3080
41	110	15	600	15 "	16.40	0.19286	0.1925
42	115	18	600	20 "	16.40	0.19286	0.1925
43	135	20	600	25 "	26.20	0.30810	0.3080

Solutions Nos. 41, 42, and 43 were twice passed through the reductor.

REDUCTION OF URANYL SOLUTIONS BY STANNOUS CHLORIDE.

These reductions were made in the same manner as iron by the Zimmerman-Reinhardt method. In some of the reductions the stannous chloride was allowed to act much longer than is ordinarily done for iron; but with the majority the procedure was the same as for iron reductions.

The color of the uranyl chloride solutions was yellow, but on continued boiling with stannous chloride it changed to green, and on still further boiling to reddish brown. When the solutions were boiled with stannous chloride, a small amount of dry sodium carbonate was added to the flask, the mouth closed by a small funnel, and the boiling continued.

When the reductions were allowed to continue for a minute or so, as for the reduction of ferric solutions, a very slight reduction occurred, but when the reduction was continued for from fifteen minutes to half an hour, the reduction approached and in several cases proceeded to the subchloride (UCl_3), the same as when a hydrochloric acid solution of uranium is reduced by either zinc, aluminum, or magnesium.

The uselessness of stannous chloride for the reduction of uranium solutions is shown by the following table:

REDUCTION OF URANYL SOLUTIONS BY STANNOUS CHLORIDE.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Minutes.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of $KMnO_4$ used. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
44, 45, 46	20	½	600	15	0.6–0.7	0.00823	0.1925
47, 48, 49	75	½	500	20	0.8–1.5	0.01764	0.1925
50, 51	75	½	500	20	0.4–0.6	0.00706	0.1925
52	35	1	550	35	0.8	0.00941	0.1925
53	50	1	550	45	2.0	0.02352	0.1925
54	35	5	600	35	16.0	0.18816	0.1925
55	50	5	600	45	18.5	0.21756	0.1925
56	75	10	600	10	4.0	0.04704	0.1925
57	75	10	600	10	8.5	0.09996	0.1925
58	35	10	600	25	11.0	0.12936	0.1925
59	30	10	600	15	15.5	0.18228	0.1925
60	30	15	600	15	20.9	0.24578	0.1925

PART III.—ESTIMATION OF URANIUM IN PITCHBLENDE.

In order to apply the preceding separations and determinations, to an actual technical assay of pitchblende, samples of the ore were analyzed by two entirely different methods: the Patera method with modifications, and the "ether extraction" method. In both cases the uranium was determined in several different ways. These assays gave an actual comparison of results, and at the same time tested the separations and estimations of uranium which were worked out on pure solutions.

The assays were first made by Patera's method as follows:

Eight samples of the finely divided ore (about 1.3 grams) were weighed into small beakers, and decomposed by adding 5 cc. water and 10 cc. nitric acid (sp. gr. 1.42). Complete solution was brought about by heating almost to boiling in covered beakers on a hot asbestos plate till the residues were almost white in color, then the watch-glasses were removed and the solutions slowly evaporated to a pasty mass. After cooling, the masses were taken up with 50 cc. water and 3 cc. nitric acid (sp. gr. 1.42), and the solution brought to boiling. The silica was filtered off and washed with boiling water and rejected. The filtrates were diluted to 200 cc. volume and hydrogen sulphide gas passed through the cold solutions for one hour. The precipitates of sulphides of lead, copper, etc., were filtered, washed with hydrogen sulphide water, and rejected. The filtrates from the sulphides were at first slowly heated, and finally boiled in order to expel hydrogen sulphide gas and to oxidize the iron. Evaporation was continued till the bulk of the solutions was about 125 cc., then the separated sulphur was filtered off and washed. The solutions were brought to boiling and 150 cc. of a saturated solution of sodium carbonate added, boiling was continued for twenty minutes, after which the precipitates (principally ferric hydroxide) were filtered off and washed three times by decantation and four times on the filter with hot water. The filtrates containing the uranium were evaporated to half volume (about 150 cc.), slowly neutralized with hydrochloric acid (sp. gr. 1.20) and about 3 cc. in excess, then boiled for half an hour till all carbon dioxide was expelled. The uranium was precipitated from the hot solutions by means of a slight excess of sodium hydroxide (free from carbonate), and boiling for about ten minutes, keeping the beakers covered with watch-glasses. The orange-yellow precipitates of sodium uranate were allowed to settle, the supernatant liquids poured through filters, and the precipitates twice washed by decantation and three times on the filters with hot water.

Precipitates Nos. 1 and 2, were dried in a hot oven, separated from the filters and ignited in platinum crucibles after which the ash of the papers was added to the crucibles and ignition continued at "redness" for five minutes. The residues on cooling were treated several times with hot water, after each treatment pouring the water through a small filter. The filters

were dried, ignited, added to the crucibles, and reignited at "redness" for ten minutes. After cooling in a desiccator, they were weighed. According to Patera, the residue consists of $NaO.2(U_2O_3)$, 100 parts of which contain 88.3 parts of U_3O_8.

Precipitates Nos. 3, 4, 5, 6, and 7 were dissolved from the filters by warm dilute hydrochloric acid (sp. gr. 1.13), and caught in small beakers. The solutions were evaporated twice to dryness on a warm asbestos plate, the second time with 10 cc. hydrochloric acid (sp. gr. 1.20). The dry residues were taken up with 3 cc. hydrochloric acid, diluted to 100 cc., and brought to boiling. The silica, dissolved from the beakers by the strong alkali solution, was filtered off, and washed with boiling water.

Solutions Nos. 3 and 4 were brought to boiling, 5 cc. hydrochloric acid (sp. gr. 1.20) added, and ammonia (sp. gr. 0.90) in excess. The solutions were boiled for fifteen minutes, thus changing the voluminous amorphous precipitate of yellow ammonium uranate into a more crystalline form, darker in color, which was readily and rapidly washed. The precipitates were allowed to settle, the supernatant liquids poured through filters, and the precipitates washed three times by decantation and twice on the filter with a hot dilute solution of ammonium chloride (2 grams of salt to 100 cc. water). The precipitates were dried, placed in platinum crucibles together with filter-paper, and slowly ignited till the paper was completely destroyed, then ignited in a blast-flame for ten minutes, after which they were slowly cooled in a gradually decreasing Bunsen flame. During ignition the crucibles were placed in a slanting position in order to allow of free circulation of air in the crucible, thus obtaining complete oxidation to U_3O_8. They were allowed to cool in a desiccator, and weighed.

Solution No. 5 was diluted to 150 cc., brought to boiling, and 5 cc. hydrochloric acid (sp. gr. 1.20) added. The solution was neutralized with ammonia (sp. gr. 0.90) and 5 cc. added in excess. Acetic acid was slowly added to the hot solution, stirring all the while, till the yellow precipitate disappeared. The uranium was then precipitated by means of ammonium dihydrogen phosphate, adding about twice as much as was necessary for complete precipitation. The solution was boiled for fifteen minutes, allowed to cool, then filtered, and the precipitate washed four times on

the filter with a hot 2 per cent. solution of ammonium chloride. The precipitate was dried, separated from the filter-paper which was first ignited in a porcelain crucible, after which the precipitate was added and ignited at low redness for ten minutes over a Bunsen flame. The crucible was allowed to cool, the residue moistened with a few drops of nitric acid (sp. gr. 1.42), dried on a hot plate, and reignited at low redness for ten minutes. The lemon-yellow colored precipitate of uranyl pyrophosphate ($(UO_2)_2P_2O_7$) was weighed, and the U_3O_8 equivalent obtained by multiplying the weight by 0.66815.

Solutions Nos. 6 and 7 were evaporated to about 30 cc. volume allowed to cool, 30 cc. sulphuric acid (sp. gr. 1.84) added, and evaporation continued to dense white fumes. The solutions were poured into 250 cc. Erlenmeyer flasks, diluted to 150 cc., and reduced at boiling temperature by about 50 grams of pure granulated zinc. The reductions were continued for one and a half hours till the solutions were a clear green color. The solutions were then poured into a large Erlenmeyer flask, which contained about one gram of dry sodium carbonate, diluted to 500 cc. and titrated by 0.01 normal potassium permanganate solution.

Precipitate No. 8, of sodium uranate, was dissolved from the filter with warm dilute nitric acid (1 part acid (sp. gr. 1.42) and 2 parts water) and caught in a small beaker. The solution was evaporated to dryness twice, the second time with 10 cc. nitric acid (sp. gr. 1.42). The dry mass was taken up with 5 cc. of 50 per cent. acetic acid, diluted to 50 cc., and the solution boiled till all salts were dissolved. The silica, which was dissolved from the beaker by the strong sodium carbonate solution, was filtered off and washed with hot water. The solution was diluted to exactly 100 cc. in a graduated flask, 50 cc. were measured into a large clean platinum dish and the uranium determined by electrolysis as follows: Added 0.5 gram sodium acetate, diluted to 125 cc. and electrolyzed at a temperature of 65° to 75° C., with a current of $N.D._{100} = 0.8$ to 1.0 ampere. The uranium was completely precipitated, as hydrated protosesquioxide, within eight hours. The electrolyte was emptied into a beaker, and the black deposit washed with warm water. The electrolyte and the washings were poured through a fluted filter-paper, the paper several times rinsed with hot water, dried, and ignited on the cover of a platinum crucible, and the ash added to the dish. The dish was

then dried, ignited over a blast-lamp for ten minutes, and allowed to cool in a gradually decreasing Bunsen flame. It was placed in a desiccator and, after thoroughly cooling, was weighed. The ignited deposit consisted of U_3O_8.

The results obtained by this series of assays are as follows :

Experiment No.	Amount of ore taken. Grams.	Weighed as :	Weight. Gram.	Calculated to U_3O_8 equivalent.	Per cent. of U_3O_8.	Average per cent.
1	1.2863	$NaO(U_2O_3)_2$	0.3064	0.27055	21.03	20.76
2	1.3278	$NaO(U_2O_3)_2$	0.3071	0.27117	20.49	
3	1.2882	U_3O_8	0.2616	0.26160	20.31	20.46
4	1.2880	U_3O_8	0.2653	0.26530	20.60	
5	1.2840	$(UO_2)_2P_2O_7$	0.3297	0.25940	20.20	20.20
6	1.4004	Titrated	....	0.29090	20.77	20.63
7	1.2164	Titrated	....	0.24940	20.50	
8	0.6416	U_3O_8	0.1306	0.13060	20.36	20.36

Estimation of Uranium in Pitchblende by the Ether Extraction Method.—The ether extraction method differs from the Patera method in that the uranium is not separated from the fourth group members by means of sodium carbonate, but by ether and by ammonium carbonate. The iron was separated from uranium and the other metals by shaking the hydrochloric acid solution with ether, free from alcohol. The uranium was then separated from the other associated metals (aluminum, manganese, zinc, and nickel) by means of ammonium carbonate.

The procedure was as follows: Seven samples (about 1.3 grams) of the finely divided pitchblende were decomposed with boiling dilute nitric acid (1 part acid (sp. gr. 1.42) and 1 part water) till the residues which remained were almost white in color. The solutions were then evaporated to a pasty mass, taken up with 15 cc. hydrochloric acid (sp. gr. 1.20), and evaporated to dryness twice, the second time with 10 cc. hydrochloric acid (sp. gr. 1.20). The salts were taken up with 5 cc. hydrochloric acid (sp. gr. 1.20), diluted to 150 cc., brought to boiling, and the silica filtered off and washed. The filtrates were diluted to 250 cc. and the lead, copper, etc., precipitated as sulphides by passing hydrogen sulphide gas through the cold solutions for about an hour. The filtrates from the sulphides were evaporated slowly to about 150 cc., and boiled for a few minutes in order to expel all hydrogen

sulphide. The separated sulphur was filtered off and washed. The solutions were brought to boiling, 5 cc. nitric acid (sp. gr. 1.42) added, and boiling continued till the iron was completely oxidized, after which ammonia (sp. gr. 0.90) was added in excess and boiling continued for fifteen minutes. The precipitates of impure ferric hydroxide, ammonium uranate, etc., were filtered off and washed with a warm 2 per cent. solution of ammonium chloride. The wet precipitates were dissolved from the filters with warm dilute hydrochloric acid (sp. gr. 1.10) and caught in small beakers. The solutions were twice evaporated to dryness, the second time with 10 cc. hydrochloric acid (sp. gr. 1.20). The dry salts were taken up with 15 cc. hydrochloric acid (sp. gr. 1.10), the beakers covered with watch-glasses, and the solutions heated till all salts had dissolved but not long enough to lose any of the acid by evaporation. After cooling, the solutions were emptied into 250 cc. separatory funnels, and the beakers rinsed out four times with 5 cc. hydrochloric acid (sp. gr. 1.10). Fifty cc. of pure ether, which had previously been shaken up with hydrochloric acid (sp. gr. 1.10), were added to each funnel, and thoroughly shaken for about seven minutes with the aqueous hydrochloric acid solutions, occasionally relieving the pressure, due to evaporation of ether. After agitation, the funnels were allowed to stand for a few minutes till the two solutions separated, then the lower aqueous layers were run into other separatory funnels. The ether layers, containing most of the iron, were twice shaken up with 5 cc. hydrochloric acid (sp. gr. 1.10) and the washings added to the main solutions containing the uranium. The second extractions were made with 50 cc. ether, and the third with 30 cc. ether. In both cases the ether solutions were twice washed with 5 cc. hydrochloric acid (sp. gr. 1.10). The aqueous hydrochloric acid solutions, now free from iron, contained a small amount of ether, which was allowed to evaporate spontaneously by exposure. They were then evaporated to about half volume (40 cc.), diluted to 100 cc., nearly neutralized with ammonia, and 100 cc. of a saturated solution of ammonium carbonate added, which precipitated all the metals except uranium. The solutions were slowly boiled for five minutes, filtered, and the precipitates washed with hot water. The filtrates were evaporated to half volume in order to get rid of most of the carbon dioxide. Yellow precipitates of ammonium

uranate separated during boiling, and were dissolved by acidifying the solutions with hydrochloric acid. The solutions were again boiled for about half an hour longer, and the uranium determined in four different ways as outlined below.

Solutions Nos. 9 and 10 were precipitated with ammonia in the same manner as solutions Nos. 3 and 4 and the uranium weighed as U_3O_8.

Solutions Nos. 11 and 12 were precipitated by an excess of ammonium dihydrogen phosphate the same as solution No. 5, and the uranium weighed as $(UO_2)_2P_2O_7$.

Solutions Nos. 13 and 14 were evaporated with sulphuric acid, reduced by metallic zinc and titrated by potassium permanganate as described under Nos. 6 and 7.

In solution No. 15, the filtrate from the ammonium carbonate precipitation was evaporated to dryness with nitric acid, and the uranium determined electrolytically as already described under No. 8.

The results obtained by the ether extraction method are as follows:

Experiment No.	Amount of ore taken. Grams.	Weighed as:	Weight. Gram.	Calculated to U_3O_8 equivalent.	Per cent. of U_3O_8.	Average per cent.
9	1.2405	U_3O_8	0.2565	0.2565	20.67	20.61
10	1.2409	U_3O_8	0.2550	0.2550	20.55	
11	1.2390	$(UO_2)_2P_2O_7$	0.3233	0.2545	20.54	20.66
12	1.2991	$(UO_2)_2P_2O_7$	0.3431	0.2701	20.79	
13	1.2892	Titration	....	0.2672	20.80	20.71
14	1.2828	Titration	....	0.2646	20.63	
15	0.6207	U_3O_8	0.1283	0.1283	20.67	20.67

A comparison of these results with those obtained by the Patera separation shows greater uniformity here. The close agreement is proof not only of the superiority of the ether extraction, method, but also of the accuracy of the methods of determination of uranium already described.

SUMMARY OF RESULTS.

The conclusions drawn from this investigation on the separation and determination of uranium, briefly stated, are as follows:

1. In order to separate uranium (and the other members of

group 4) from the metals of groups 5 and 6, the solution should contain not over one part of concentrated acid (either hydrochloric or nitric acid) in fifty parts of solution.

2. The separation of uranium from the metals of groups 3 and 4 is best accomplished by means of either a saturated solution of sodium carbonate, or else by ether followed by a saturated solution of ammonium carbonate. The latter method is preferable when the introduction of fixed alkalies and silica is undesirable.

3. The ether extraction method for the separation of uranium from iron depends on the fact that ferric chloride is extracted from an aqueous hydrochloric acid solution, whereas the uranyl chloride is retained in the aqueous solution. For this separation it is necessary that the hydrochloric acid used for the solution be of 1.10 specific gravity and that three ether extractions be made. The ether used should be free from alcohol, and also previously shaken up with hydrochloric acid (sp. gr. 1.10).

4. The separation of uranium from iron by means of sodium carbonate is complete, provided a large excess of a saturated solution of sodium carbonate be used, and the solution boiled for at least fifteen minutes after the precipitation. The boiling is necessary in order to get all the uranium into solution. By such treatment, no uranium remains with the iron, which is completely precipitated as ferric hydroxide in a form readily filtered and washed.

5. The separation of uranium from the alkalies and alkaline earths by means of electrolysis is complete, easily accomplished and gives accurate results.

6. The separation of uranium from the alkalies and alkaline earths is accomplished by precipitating the uranium three times from a hot solution with ammonia in the presence of ammonium chloride.

7. The separation of uranium from the alkalies and alkaline earths by means of an excess of ammonium phosphate in the presence of ammonium acetate is complete. The precipitations should be made from a hot solution and the boiling continued for at least fifteen minutes.

8. The yellow slimy amorphous precipitate of an ammonium uranate, formed by precipitating uranium with ammonia in the presence of an ammonium salt, is converted into a darker crystalline form by boiling it for about twenty minutes, and then allowing it to settle in the cold.

9. The separation of the filter-paper from the precipitate of ammonium uranate for the purpose of igniting to UO_2 or U_3O_4 is unnecessary.

10. The complete oxidation of uranium to U_3O_8 is accomplished by igniting ammonium uranate, in either a platinum or porcelain crucible, over a blast-lamp. This is done by having the crucible in a slanting position and igniting intensely over a blast-lamp for about ten minutes, after which the crucible is allowed to cool in a slowly decreasing Bunsen flame.

11. The reduction of U_3O_8 to UO_2, as recommended by Rose for the purpose of control, was found unreliable.

12. The estimation of uranium as phosphate is easily and accurately done when the precipitant used is ammonium phosphate, in the presence of ammonium acetate. The precipitate of $UO_2NH_4PO_4$ on boiling becomes crystalline, and is easily filtered and washed. The ignited precipitate previous to weighing should be moistened with nitric acid (sp. gr. 1.42), dried and reignited at low redness in a porcelain crucible. Above this temperature, and especially so in platinum, a reduction of the $(UO_2)_2P_2O_7$ always occurs. Whenever this happens it may be reoxidized to $(UO_2)_2P_2O_7$ by moistening the greenish mass with nitric acid (sp. gr. 1.42) and reigniting at low redness. The ignitions should be done in porcelain.

13. The most rapid determination of uranium is accomplished by reducing a sulphate solution by means of pure metallic zinc and titrating it with standard potassium permanganate solution in an atmosphere of carbon dioxide. The reductions, whether made by means of metallic zinc, aluminum, magnesium, or in a long Jones reductor, were in all cases complete, and the results obtained were concordant with those obtained gravimetrically.

14. When hydrochloric acid solutions of uranium are reduced by means of metallic zinc, aluminum or magnesium, the reduction goes lower than UCl_4. It approached and in several cases reached the subchloride UCl_3. When stannous chloride is used the results are utterly unreliable; so no reduction of uranium in an hydrochloric acid solution can be used for the estimation of uranium.

This work was suggested by Dr. Edmund H. Miller, and carried out under his direction.

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METHODS OF STANDARDIZING ACID SOLUTIONS.

By Cyril G. Hopkins.

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THE recent articles on "The Preparation of an Exact Standard Acid" and "The Electrolysis of Copper Sulphate as a Basis for Acidimetry," by Higgins[1] and Kohn,[2] respectively, both of whom appear to have overlooked the fact that this electrolytic method for standardizing acids was introduced by Hart and Croasdale[3] more than ten years ago, have suggested that a series of results obtained by the writer, in a comparative study[4] of "Methods of Standardizing Reagents Used in Acidimetry and Alkalimetry," would add something of interest and value on the subject, especially to such as are interested in volumetric analysis.

The special object in this study was to determine the most exact method of standardizing a solution of acid for subsequent use as "standard acid," this being the ultimate and practical purpose of any basis for acidimetry.

Six different methods of standardizing acid solutions were investigated and compared:

1. The silver chloride method of standardizing hydrochloric acid with some modifications and improvements as to manipulation.

2. The method of standardizing sulphuric acid by weighing as ammonium sulphate, as recommended by Wenig.[5]

3. The method of using metallic sodium, introduced by Hartley[6] and improved by Neitzel.[7]

4. The method of standardizing acids by use of pure crystallized borax.

5. The method based upon the electrolysis of copper sulphate, introduced by Hart and Croasdale[8] and strongly recommended by Hart[9] and recently rediscovered by Kohn.[10]

[1] *J. Soc. Chem. Ind.*, **19**, 958 (1900).

[2] *Ibid.*, **19**, 962 (1900).

[3] *J. Anal. Chem.*, **4**, 424 (1890).

[4] Author's unpublished thesis for the degree of Master of Science, Cornell University, 1894. Acknowledgment is made of valuable suggestions from Dr. G. C. Caldwell, under whose supervision this work was done.

[5] *Ztschr. angew. Chem.*, (1892), 204.

[6] *Quar. Jour. Chem. Soc.*, **26**, 123 (1873).

[7] *Ztschr. anal. Chem.*, **32**, 422 (1893).

[8] *J. Anal. Chem.*, **4**, 424 (1890).

[9] *Ibid.*, **6**, 421 (1892).

[10] *J. Soc. Chem. Ind.*, **19**, 962 (1900).

6. The method of standardizing oxalic acid by means of metallic iron and potassium permanganate.

Before the details of the results obtained in this work are considered, it is desired to call attention to two questions which have important effects upon accuracy in different methods of standardizing:

1. Is the method of standardizing direct or indirect?

2. Is the actual error which may be made in the determination of the substance which is brought to the balance mathematically increased or diminished by computing to the equivalent amount of the acid standardized?

In considering the first question a classification may be made of (1) direct, (2) indirect, and (3) doubly indirect methods, the direct methods requiring only a gravimetric determination, the indirect requiring a gravimetric and a volumetric determination, or a weighing and a titration, and the doubly indirect methods requiring one weighing and two titrations.

The silver chloride and ammonium sulphate methods are direct, the chlorine being precipitated and weighed as silver chloride, and the sulphuric acid being neutralized and weighed as ammonium sulphate.

The metallic sodium and borax methods are indirect, the sodium and the borax each being weighed and then, after being put in solution, titrated to standardize the acid.

The copper sulphate and iron-permanganate methods are doubly indirect, each requiring one weighing and two titrations. The copper is deposited and weighed, the small amount of sulphuric acid liberated titrated against an alkaline solution, and this in turn titrated to standardize the permanent acid solution. The iron is likewise weighed, then put into solution, titrated against permanganate solution, and this solution titrated against the oxalic acid.

To answer the second question we must compare the weight of the substance which is brought to the balance with the weight of the equivalent (but not equal) amount of the standard acid. In all of the methods, one of the numbers from which the strength of the standard acid is calculated is obtained by using the balance. The substance weighed is our real basis for computation. In the two direct methods it is silver chloride and ammonium sulphate; in the indirect methods it is sodium and borax, and in the doubly

indirect methods it is copper and iron. The accuracy of the manipulation and the purity of the substance are important factors in obtaining correct weights of these substances, and the ratio which a given quantity of the weighed substance bears to the equivalent amount of the acid standardized is an important consideration. Following is a tabular statement arranged to show a comparison of these ratios in the six methods, the numbers being determined by the reactions in each case and reduced to the basis of monobasic acid :

Substances weighed.	Equivalent weights of acid.	Ratios existing.
143.39 AgCl	36.46 HCl	1 : 0.25
66.10 $(NH_4)_2SO_4$	49.04 H_2SO_4	1 : 0.74
23.06 Na	36.46 HCl	1 : 1.58
191.15 $Na_2B_4O_7.10H_2O$	36.46 HCl	1 : 0.19
31.80 Cu	49.04 H_2SO_4	1 : 1.54
	36.46 HCl	1 : 1.15
56.00 Fe	45.01 $H_2C_2O_4$	1 : 0.80

From this table it can be seen that an error of 1 mg. in the purity or in the manipulation in securing the weight of the sodium would cause an error of 1.58 mg. in the equivalent amount of standard hydrochloric acid ; while the same error, 1 mg., in obtaining the weight of borax would cause an error of only 0.19 mg. in the equivalent amount of standard acid. In other words, an error of 1 mg. in obtaining the weight of sodium would have the same influence on the accuracy of the determination of the strength of the standard acid as would an error of 8.3 mg. in obtaining the weight of borax, equivalent amounts of each (sufficient to neutralize the same quantity of acid) being taken. Similarly, 1 mg. error in obtaining the weight of copper would have the same influence on standard sulphuric acid as would an error of 6.2 mg. in the weight of silver chloride on standard hydrochloric acid. These are certainly considerations which should be taken into account, as they may very materially affect the possible accuracy of methods.

Following are statements of results obtained by each method with as brief descriptions as seem practicable of processes of manipulation :

1. *Silver Chloride Method.*—Standardizing hydrochloric acid by precipitating with silver nitrate and weighing the silver chloride.

A solution of hydrochloric acid of about one-fourth normal strength was prepared for standardizing. Portions of the acid solution were measured out with a pipette, the exact capacity of which was found by calibration with mercury to be 50.06 cc. The solution was delivered into a 250 cc. Erlenmeyer flask provided with a clean, smooth, close-fitting, solid rubber stopper, the pipette being rinsed with a few cubic centimeters of pure water (which was added to the measured acid), and then dried before again being used. All measurements were reduced[1] to a uniform temperature of 20° C.

A sufficient quantity (as determined by stoichiometric computation) of a 5 per cent. solution of silver nitrate to nearly, but not quite completely, precipitate all of the chlorine, was at once added, the necessary additional quantity being added in less than 1 cc. portions. The flask was closed with a rubber stopper[2] and shaken after each addition, so that the precipitate would settle and it could easily be known when sufficient precipitant had been added, a large excess of silver nitrate, which would possess some solvent action on the silver chloride and necessitate much washing for its complete removal from the precipitate, thus being avoided.

After the precipitation was complete, the flask was shaken until, after standing a short time, the supernatant liquid became perfectly clear. It was then allowed to stand in an inclined position until the precipitate settled down quite compactly in the bend of the flask. The solution was then poured off through a Gooch crucible as completely as possible without transferring more than a mere trace of the precipitate. The flask was then set aside in an inclined position, such that the precipitate was not at the lowest point, where the remaining liquid would collect. After two or three minutes the liquid, which had drained out of the precipitate, was also poured through the filter. About 100 cc. of pure water containing a trace of nitric acid,[3] sufficient only to make it distinctly acid, were now poured into the flask, which was then closed and thoroughly shaken, the precipitate allowed to settle, and the liquid twice decanted just as before. This

[1] Schulze: "Expansion of Liquids in Glass Vessels," *Ztschr. anal. Chem.*, **21**, 167 (1882).

[2] Whenever the stopper is removed it must, of course, be carefully rinsed off into the flask.

[3] In perfectly pure water, silver chloride does not cohere well, but remains persistently in very fine particles; indeed, after it has been well collected in large particles by being shaken in an acid solution, it will separate again into fine particles if shaken with pure water.

treatment was repeated with another 100 cc. of the wash-water, after which the precipitate was again shaken with the wash-water and then transferred to the crucible. The last traces are quickly and easily and completely transferred, simply by the use of a good "spritz" bottle, the flask being inclined mouth downward over the crucible and rotated during the operation. The "transfer" wash-water gave no test for silver.[1] The precipitate was heated in the air-bath at 130° to 150° to constant weight.

Six determinations gave the following results:

	Solution taken. cc.	Temperature.	AgCl found. Gram.	AgCl from 50.06 cc. at 20°. Gram.	HCl in 1 cc. at 20°. mg.
1	50.06	20.0°	1.9310	1.9310	9.808
2	50.06	20.0°	1.9312	1.9312	9.809
3	50.06	23.5°	1.9295	1.9310	9.808
4	50.06	23.5°	1.9292	1.9307	9.807
5	50.06	22.0°	1.9301	1.9309	9.808
6	50.06	22.0°	1.9301	1.9309	9.808

Another solution of hydrochloric acid of slightly greater strength was subsequently standardized by using the method just described, and in doing this work an attempt was made to determine the exact loss of silver chloride (if there be any loss) incurred by this method of washing. In the following determinations, Nos. 1, 2, 3, and 4 were washed exactly as described above, while Nos. 5 and 6 were washed just five times as much by exactly the same method of washing. Regularly three portions of 100 cc. each of liquid are decanted from the precipitate, and the precipitate is then transferred with a 100 cc. portion of wash liquid; but in Nos. 5 and 6 (below) this fourth 100 cc. portion was also decanted each time until the last of the five complete washings, when, of course, it was used in transferring the precipitate. Furthermore, in order that the solvent action of the five complete washings should produce an effect equal to five times the effect of the one necessary washing, an addition of 1 cc. of the silver nitrate solution was made to the first 100 cc. of wash-water used in each of the four extra washings.

[1] When working with duplicates this method of washing by thorough decantation takes little extra time, and not more than 1 or 2 cc. of liquid will be left in the precipitate. The excess of silver nitrate solution added in the precipitation contains only about 50 mg. of silver nitrate, and the volume of liquid, when the precipitation is complete, is at least 100 cc. Suppose that 5 cc. of this remains with the precipitate after shaking and decanting; by theory this should retain only 2.5 mg. of silver nitrate. After the second 100 cc. is decanted, about 0.1 mg. of silver nitrate would be left in the flask, and, after the third decantation, only 0.005 mg., an unweighable quantity, of silver nitrate would remain with the silver chloride precipitate. The fact that not a trace of silver was found in the wash-water after the transfer of the precipitate proves this theory correct in practice.

Six determinations gave the following results :[1]

	HCl in 1 cc. at 20°. Mg.
1	10.297
2	10.295
3	10.296
4	10.295
5	10.297
6	10.292

The results show that there is certainly no appreciable loss of silver chloride by this process of washing.

These twelve results (in two sets) include all of the determinations which were made by the method just described ; in other words, all results obtained are here reported. These results and seven years of subsequent experience[2] with the method lead me to confidently assert that by this method a skilled manipulator can easily and quickly make determinations of hydrochloric acid within a limit of error of 0.5 mg. of silver chloride on 2 grams of precipitate.

2. *Ammonium Sulphate Method.*—Standardizing sulphuric acid by neutralizing the acid solution with ammonium hydroxide, evaporating to dryness, and weighing the ammonium sulphate. This was first recommended in 1892 by M. Wenig.[3]

A solution of about one-fourth normal sulphuric acid was used. Portions of 50.06 cc. were measured out and delivered into a weighed platinum dish. Ammonium hydroxide was then added in slight excess, the solution evaporated to dryness on the water-bath, and the residue dried to constant weight at 120°.

The ammonium hydroxide was distilled just before using. The sulphuric acid was free from nitrogen and the residue of ammonium sulphate was completely volatile upon gentle ignition, showing the absence of fixed bases.

Six determinations of the sulphuric acid in the standard solu-

[1] These figures are taken from a copy of the thesis already referred to. The laboratory note-book in which the full record of the determinations was preserved has been subsequently lost in a fire, hence the complete data, including weights of silver chloride, etc., cannot be given.

[2] The following are duplicate determinations on four different solutions of hydrochloric acid which have been standardized in the course of ordinary work (weights of silver chloride are given) :

		1. Grams.	2. Grams.	3. Grams.	4. Grams.
AgCl found	1	1.4103	1.4062	1.2173	1.2296
	2	1.4104	1.4064	1.2177	1.2295

[3] *Zischr. angew. Chem.*, 1892, p. 204.

tion were made by this method, with the following results (in No. 2 a slight mechanical loss of ammonium sulphate occurred):

	Solution taken. cc.	Temperature.	$(NH_4)_2SO_4$ found. Gram.	$(NH_4)_2SO_4$ from 50.06 cc. at 20°. Gram.	H_2SO_4 in 1 cc. at 20°. mg.
1	50.06	19.5°	0.7808	0.7807	11.570
2	50.06	19.5°	0.7795 (?)	0.7794 (?)	11.549 (?)
3	50.06	20.5°	0.7806	0.7807	11.570
4	50.06	20.5°	0.7809	0.7810	11.574
5	50.06	19.0°	0.7809	0.7807	11.570
6	50.06	19.0°	0.7808	0.7806	11.569

No. 2 being omitted, these weights of ammonium sulphate from 50.06 cc. of solution, at 20°, agree within 0.4 mg. on nearly 0.8 gram of residue and they indicate that this method of standardizing sulphuric acid is exceedingly accurate. The method is certainly simple and rapid. A comparison of the results obtained by this and the other methods is given below.

3. *Sodium Method.*—Standardizing acids by the use of metallic sodium.

The use of metallic sodium as a basis for acidimetry was first recommended in 1873 by Hartley.[1] In 1893 Neitzel[2] suggested that the sodium be weighed under petroleum in a small beaker instead of in weighing-tubes as recommended by Hartley.

I found a small glass-stoppered weighing-bottle to be an improvement over the beaker, as the petroleum is appreciably volatile at the ordinary temperature. The petroleum was distilled over sodium before being used, that portion being taken which distilled above 200°.

The sodium was cut out as rapidly as possible from a block of the metal, a piece with clean metallic surfaces being thus obtained. With a pair of forceps, it was quickly placed into a weighing-bottle containing sufficient petroleum to cover it. After being weighed, the sodium was dissolved in neutral alcohol in an Erlenmeyer flask which was connected with a reflux condenser. The solution was diluted with water (poured in through the condenser tube) and then titrated against standard acid.

Phenolphthalein was used as an indicator, giving a very sharp and satisfactory "end-reaction."

The burette used was carefully calibrated and the burette readings were taken to hundredths of a cubic centimeter as accurately as possible.

[1] *Quar. J. Chem. Soc.*, **26**, 123 (1873).
[2] *Ztschr. anal. Chem.*, **32**, 422 (1893).

Six determinations gave the following results :

	Metallic sodium taken. Gram.	Acid (HCl) solution required. cc.	Temperature.	Acid solution required at 20°. cc.	Acid solution at 20° required for 0.7154 gram sodium.[1] cc.	HCl in 1 cc. at 20°. mg.
1	0.8853	142.10	23.5°	142.00	114.75	9.857
2	0.6358	101.95	23.5°	101.88	114.63	9.867
3	0.9352	150.45	27.0°	150.21	114.91	9.843
4	0.7004	112.40	26.0°	112.25	114.65	9.865
5	0.6229	100.00	22.0°	99.96	114.80	9.853
6	0.5128	82.47	23.0°	82.42	114.98	9.837

As standardized by the silver method (average of six determinations) this acid contained in 1 cc. 9.808 mg. hydrochloric acid.

The following two determinations (only) were made to standardize the sulphuric acid solution by use of metallic sodium. The results follow :

	Metallic sodium taken. Gram.	Acid (H_2SO_4) solution required. cc.	Temperature.	Acid solution required at 20°. cc.	Acid solution at 20° required for 0.51445 gram sodium.[2] cc.	H_2SO_4 in 1 cc. at 20°. mg.
1	0.4750	86.85	23°	86.80	94.01	11.637
2	0.5539	101.25	23°	101.19	93.98	11.641

As standardized by the ammonium sulphate method (average of the five trustworthy determinations) this acid contained in 1 cc. 11.571 mg. sulphuric acid.

It will be observed that the results obtained by the sodium method, with both hydrochloric and sulphuric acids, agree well among themselves, considering that they are obtained by an indirect method which includes volumetric determinations. But it will also be observed that the results obtained by the sodium method are invariably higher than those obtained by the silver chloride and the ammonium sulphate methods. Without doubt this discrepancy is due to impurities contained in the sodium itself. Traces of carbon and iron were easily detected, and the presence of potassium was revealed by the spectroscope. The presence of elements of higher equivalent weights than sodium was indicated by converting the metal to sulphate. Two determinations gave 3.0783 and 3.0781 grams sulphate per gram of metal taken, while by theory 1 gram sodium is equivalent to 3.0829 grams sodium sulphate. Iron and potassium would each

[1] Average amount taken. The number of cubic centimeters given in this column are computed for each separate determination to show in cubic centimeters the limit of error in the titrations.

[2] See previous foot-note.

retain a smaller proportion of sulphuric acid radical than would sodium, while the carbon would be oxidized and lost.

Although the sodium used in this work was shown to be not perfectly pure and its titrating value to be not absolutely correct, so that results of the highest exactness could not be obtained by using the sodium as a substance with which to standardize acids, nevertheless its titrating value was, of course, constant whether used against hydrochloric or sulphuric acid ; and, by considering the strength of the standard sulphuric acid as determined by the ammonium sulphate method, the relation found between the sulphuric acid and sodium, and that found between the sodium and the hydrochloric acid, we have all the necessary data for computing the strength of the hydrochloric acid determined by a doubly indirect method (based upon the ammonium sulphate determinations), independent of the silver method or the sodium method.

By using the average of the five satisfactory determinations of sulphuric acid, and the average of the two titrations of the sulphuric acid against sodium and then computing through the six separate titrations of sodium against hydrochloric acid, I obtain the following values (column 1) for 1 cc. of the hydrochloric acid solution (column 2 gives the results obtained by the direct silver chloride method, and column 3 those obtained by the regular sodium method).

HCl IN 1 CC. SOLUTION AT 20°.

	1. Doubly indirect ammonium sulphate method.	2. Direct silver chloride method.	3. Indirect sodium method.
1	9.799	9.808	9.857
2	9.809	9.809	9.867
3	9.785	9.808	9.843
4	9.807	9.807	9.865
5	9.793	9.808	9.853
6	9.780	9.808	9.837

It is interesting to observe that, within the limits of error in titration, the results which are based upon the ammonium sulphate method are in perfect agreement with those obtained by the direct silver chloride method.

4. *Borax Method.*—Standardizing acids by the use of crystallized borax.

This method is recommended by Rimbach,[1] by whom the

[1] *Ber. d. chem. Ges.*, **26**, 171 (1893).

method was also employed in his work on the atomic weight of boron.[1]

In the following work, C. P. borax was dissolved in water by the aid of heat. As the solution cooled, crystals began to form at about 45°. When the temperature had fallen to 30°, the mother-liquor was drained off, the crystals washed with cold water, placed on drying paper, and dried at the room temperature for four days, being turned occasionally to insure thorough drying. To standardize an acid, the crystallized borax is simply weighed, dissolved in water, and titrated against the acid. The standard hydrochloric acid mentioned as having been standardized by the silver chloride method and found by six closely agreeing determinations to contain 10.295 mg. hydrochloric acid in 1 cc. at 20°, was used in this work.

Ten determinations by means of borax were made, four after four days' exposure to the air, four after five days', and two after six days' exposure, the titrations always being made with the hydrochloric acid solution at 20°. Litmus, as recommended by Salzer,[2] was used as an indicator in the first four titrations; but the end-reaction was not sharp, and in the subsequent titrations dimethyl orange, as Rimbach recommends, was used. It was very satisfactory.

	$Na_2B_4O_7.10H_2O$ taken. After four days. Grams.	Acid required at 20°. cc.	Acid solution at 20° required for 5.4944 grams borax.[3] cc.	HCl in 1 cc. at 20°. mg.
1	5.3481	99.1	101.81	10.294
2	5.5075	102.1	101.86	10.289
3	5.3044	98.4	101.92	10.282
4	5.2896	98.1	101.90	10.284
	After five days.			
5	5.4370	101.05	102.13	10.263
6	5.5977	104.05	102.13	10.262
7	5.4045	100.37	102.04	10.271
8	5.4906	102.05	102.12	10.262
	After six days.			
9	5.2891	98.60	102.43	10.231
10	6.2754	117.05	102.47	10.226

Although the results obtained on one and the same day agree well with themselves, especially when dimethyl orange was used as the indicator; yet the results indicate that the borax is not

[1] *Ber. d. chem. Ges.*, **26**, 164 (1893).
[2] *Zischr. anal. Chem.*, **32**, 529 (1893).
[3] Average amount taken.

constant, but that it continually loses water of crystallization. To test this point further, samples of the borax which had been dried by exposure to the air for six days were weighed out and allowed to stand, exposed to the air but protected from the dust.

Following are the weights of the two samples on several subsequent days :

No. of days drying.	Weight of borax. 1. Grams.	2. Grams.
6	9.2214	10.0762
7	9.2132	10.0646
9	9.1920	10.0396
10	9.1738	10.0135

It is evident that the borax continually lost water of crystallization whether exposed to the air on drying paper or kept in open vessels. Rimbach found that crystallized borax remained constant after three or four days' drying, if kept in the air at the ordinary temperature, but that it lost weight readily when placed in dry air. Of course if the temperature and humidity of the air were such that the vapor-pressure of the atmospheric moisture exceeded that of crystallized borax, then the salt would not effloresce ; and Rimbach may possibly have worked under such conditions.

Copper Sulphate Method.—Standardizing acids by use of the sulphuric acid set free in the electrolysis of copper sulphate. This method was introduced by Hart and Croasdale[1] in 1890. It consists in subjecting a solution of pure copper sulphate to electrolysis, weighing the copper deposited, titrating the liberated acid against an alkaline solution, and then using the alkali in standardizing a permanent acid solution. It is thus a doubly indirect method.

In the following work platinum dishes were used for the negative electrodes. The strength of current used corresponded to about 3.5 cc. of oxyhydrogen gas per minute. The acid set free was titrated against approximately one-tenth normal solution of sodium hydroxide made from metallic sodium. The alkali was then titrated against standard hydrochloric acid.

The copper sulphate was tested for acidity with methyl orange and found to be perfectly neutral. Tests for other bases than copper gave negative results. After the liberated acid had been

[1] *J. Anal. Chem.*, 4, 424 (1890).

transferred and the platinum dish well rinsed with pure water, the deposited copper was washed with absolute alcohol and the dish dried at the temperature of the hands, excepting in determinations 1 and 2, in which the alcohol was drained out well and the last traces burned out as directed by Hart and Croasdale. In determination 2, some of the copper turned bluish green, indicating the formation of a salt of copper combined with some intermediate acid product of combustion. Because of this fact No. 2 is not considered a trustworthy determination.

Because of the large influence on the accuracy of the final results of any error in weighing the copper the weights were all taken by the method of oscillations.[1] The relation between the standard hydrochloric acid and the sodium hydroxide solutions was determined by titration as follows :

1	50.06 cc. acid	required	119.37 cc. alkali.
2	50.06 " "	"	119.45 " "
3	50.06 " "	"	119.41 " "
Average 1	" "	"	2.3853 cc. alkali.

Following are the results of eight determinations of the strength of a standard hydrochloric acid as ascertained by means of the copper sulphate method :

	Copper deposited from $CuSO_4$. Gram.	NaOH solution required to neutralize the liberated H_2SO_4. cc.	HCl solution equivalent at 20°. cc.	HCl in 1 cc. at 20° mg.
1	0.15349	42.85	17.964	9.796
2	0.16664 (?)	45.78	19.192	9.954 (?)
3	0.15596	43.45	18.216	9.793
4	0.14853	41.35	17.336	9.823
5	0.16719	46.58	19.528	9.815
6	0.14921	41.57	17.428	9.816
7	0.16468	45.80	19.201	9.833
8	0.19207	53.68	22.505	9.785

The following table gives a series of results obtained by Hart and Croasdale[2] in standardizing a solution of sulphuric acid by this method, and, for comparison, the results of my own determinations as just given (except that they are reduced to 0.5 cc. acid solution to make the results more comparable, my acid being very much stronger than theirs); and also my results obtained on the same acid solution by the direct silver chloride method, and on a

[1] Kohlrausch's "Physical Measurements," p. 23, (1891).

[2] *J. Anal. Chem.*, 4, 426 (1890).

sulphuric acid solution by the ammonium sulphate method (also reduced to 0.5 cc.).

Hart and Croasdale. Copper sulphate method, H_2SO_4 in 1 cc. mg.	Hopkins. Copper sulphate method, HCl in $\frac{1}{2}$ cc. mg.	Hopkins. Silver chloride method, HCl in $\frac{1}{2}$ cc. mg.	Hopkins. Ammonium sulphate method, H_2SO_4 in $\frac{1}{2}$ cc. mg.
4.814	4.898	4.904	5.785
4.802	4.897	4.905	5.785
4.791	4.912	4.504	5.787
4.799	4.908	4.904	5.785
4.819	4.908	4.904	5.785
4.811	4.917	4.904	....
4.767	4.893	....	....
Maximum variation 0.052	0.024	0.001	0.002

The copper sulphate method of standardizing acids gives fairly satisfactory results, but it falls far short of the direct silver chloride and ammonium sulphate methods in accuracy. The reason for this is found both in the substances used and in the number of manipulations. First, the ratio of the substance weighed to the acid determined is such that an error in obtaining the weight of copper vitiates the final result five or six times as much as an equal error in weighing silver chloride, and twice as much as an equal error in weighing ammonium sulphate. Further, the amount of copper which can be conveniently deposited in suitable condition for washing and weighing is relatively and absolutely smaller than the amounts of silver chloride or of ammonium sulphate conveniently manipulated. But the still more serious objection to the method is the fact that, even after the weight of copper is obtained, two volumetric determinations are necessary before the strength of the permanent acid solution can be ascertained.

In a second paper[1] on "Copper Sulphate as a Material for Standardizing Solutions," Dr. Hart appears to have overlooked these objections, as may be seen from the following quotation:

"A committee of the Association of Official Agricultural Chemists have compared our method (Hart and Croasdale's method) with others, and speak well of it. I doubt whether their report adds to the evidence in either direction, however, since their ultimate standard was a solution of hydrochloric acid, the strength of which was determined with silver nitrate. Every chemist

[1] *J. Anal. Appl. Chem.*, **6**, 421 (1892).

knows, however, that it is an easy matter to make an error of half a milligram in any method involving a precipitation and the transfer of a precipitate ; Croasdale's results and those of Richards show that the error involved is much less when copper is determined by the battery method, and that we can probably determine copper more accurately than any other element, consequently that our method should be taken as the standard and others referred to it."

No question need be raised in regard to the exactness of the electrolytic assay of copper. It is a direct and absolute method for the determination of copper, but the method, based upon that determination, of using the liberated acid for standardizing a permanent acid solution by making two volumetric determinations, and computing from the low equivalent weight of copper (as compared with that of silver chloride) is very indirect and not exceedingly accurate; and this comparative study of methods of standardizing acids has convinced the writer that the objections mentioned to the copper sulphate method are applicable and valid; also that the silver chloride method (as described) and the ammonium sulphate method are extremely accurate and satisfactory for standardizing solutions of hydrochloric and sulphuric acids, respectively.[1]

UNIVERSITY OF ILLINOIS.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 32.]

SOME EXPERIMENTS WITH THE MONONITROORTHOPHTHALIC ACIDS.

BY MARSTON TAYLOR BOGERT AND LEOPOLD BOROSCHEK.

Received August 1, 1901.

ALTHOUGH both mononitro-*o*-phthalic acids have long been well known, yet, of their derivatives, with the exception of their salts and esters, only the anhydride, imide, and anil have been described. It seemed, therefore, of interest to prepare some of the other derivaties of these acids and to study their properties, and the present paper records our first experiments along this line.

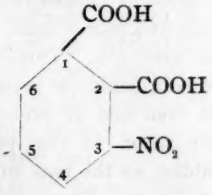
[1] The iron-permanganate method gave fairly accurate results as a method for standardizing oxalic acid. It is no more indirect and no less accurate (if the purity of the iron be known) than the copper sulphate method. It is thought that a detailed description here of the work done upon the iron-permanganate method would not be of special interest or value.

Naturally, the first question to be decided was as to the best method for the preparation of the pure acids themselves. Our experience has shown that the direct nitration of phthalic acid itself, or of its anhydride, gives good yields of the pure 3,nitro-*o*-phthalic acid, but that as a method for the preparation for the isomeric 4,nitro acid it is not so good as that depending upon the oxidation of *p*-nitrophthalide with alkaline potassium permanganate.

Of the derivatives of the 3,nitro-*o*-phthalic acid, we have prepared and studied the acid aniline and *o*-toluidine salts, a new acid ethyl ester, the imide, amide, amidic acid, ethylimide, anil, anilic acid, ortho-, meta-, and paranitranils, ortho-, meta-, and paratolils, and the hydrazide.

Of the 4,nitro-*o*-phthalic acid, the following derivatives are described: Acid aniline salt, a new acid ethyl ester, anhydride, imide, amide, amidic acid, ethylimide, anil, anilic acid, ortho-, meta-, and paranitranils, ortho-, meta-, and paratolils, *p*-tolilic acid, and hydrazide; also the corresponding azophthalic acid and azophthalide.

By the action of phosphorus pentachloride upon the anhydride of the 3,nitro-*o*-phthalic acid, the anhydride of the 3,chlor-*o*-phthalic acid was formed, and from this the free acid and imide were prepared.



α, OR 3,NITRO-*o*-PHTHALIC ACID.

Preparation of the Acid.

Method of Beilstein and Kurbatow.[1]—One part of α-nitronaphthalene is dissolved in 7 parts of 90 per cent. acetic acid, and 5 parts of chromic anhydride gradually added. When the reaction is over, dilute with water, filter out unchanged nitronaphthalene, extract the filtrate with chloroform, to remove nitrophthalide,[2] boil the acetic acid solution with barium carbonate, decompose

[1] *Ann. Chem.* (Liebig), **202**, 217 (1880).
[2] *Ber. d. chem. Ges.*, **18**, 3452 (1885).

the precipitated barium nitrophthalate with sodium carbonate, acidify with sulphuric acid, collect the liberated nitrophthalic acid in ether, evaporate the ether, and crystallize the residue from water.

We have found this method unsatisfactory for several reasons. In the first place, the reaction proceeds with considerable violence, prohibiting the use of large amounts of materials, while attempts to moderate its violence only result in the formation of more resinous by-products, as was likewise the experience of Beilstein and Kurbatow;[1] yet, in spite of the apparent energy of the reaction, considerable of the nitronaphthalene is recovered unchanged, in some cases as much as 25 per cent. Then, the method is rather long and tedious, the yield small (25 per cent. of theory) and the quality of the resulting acid poor, the crystals invariably showing a low melting-point and carrying a small amount of a red coloring-matter from which they are freed with difficulty.

Method of Miller.[2]—This is the process generally employed for the simultaneous preparation of both nitro-*o*-phthalic acids. It is as follows:

Fifty grams of *o*-phthalic acid are nitrated in a roomy flask by a mixture of 75 grams concentrated sulphuric acid and 75 grams fuming nitric acid, the flask being heated two hours upon the water-bath. The result of this nitration is a mixture of the two nitro-*o*-phthalic acids and picric acid, together with unchanged phthalic acid, acetic acid, etc. Towards the close of the heating some of the 3,nitro acid begins to separate in prisms. The mass is then allowed to cool and is precipitated by the addition of water. The composition of the precipitate varies with the amount of water added, as the two nitro-*o*-phthalic acids possess very different solubilities in dilute mineral acids: 240 cc. of water precipitate mainly the 3,nitro acid, while half this amount throws down the 4,nitro acid also. This difference in solubility cannot, however, be used as a means of separation (for the 4,nitro acid, at least), since picric acid remains in solution with the 4,nitro acid and combines with it in recrystallization; hence, it is better to precipitate both nitrophthalic acids together, although some picric acid is thus always carried down, apparently in union with the 4,nitro acid. The reaction mixture is, therefore, diluted

[1] *Loc. cit.*

[2] *Ann. Chem.* (Liebig), **208**, 223 (1881).

with 120 cc. of water, allowed to stand twelve hours in a cool place, the precipitate filtered out upon cloth, and the acid mother-liquor removed as completely as possible by suction and pressure. The precipitate is then rubbed up with a little water and extracted repeatedly with ether. The first ether extracts contain mainly the 4,nitro acid and picric acid, and are, therefore, yellow in color, while the more difficultly soluble 3,nitro acid is extracted last. Evaporation of the ether leaves a yellow acid mixture, melting at 154°–186°, in a yield of 85 per cent. of the theory, from which the 3,nitro acid may be obtained by frequent crystallization from water, the 4,nitro acid and picric acid remaining in the mother-liquors. The yield of pure 3,nitro acid thus obtained is about 50 per cent. of the weight of the crude acid mixture.

As pointed out by Miller,[1] this process can be considerably shortened if it is not desired to recover the 4,nitro acid, by taking the first precipitate of crude acids, removing the mineral acids by careful washing, pressing, and draining upon a clay plate, and then separating the difficultly soluble 3,nitro acid by crystallizing this cake repeatedly from water.

In carrying out this method, the phthalic acid dissolves after about a half hour's heating, to a clear amber solution, with evolution of copious fumes of oxides of nitrogen. After heating for about an hour longer, the 3,nitro acid begins to crystallize out, and the contents of the flask soon change to a mass of crystals. Sufficient water is then added to precipitate mainly the 3,nitro acid, the mixture is allowed to stand twenty-four hours in a cool place, and the precipitate then separated as thoroughly as possible from the acid mother-liquor, giving a cake of crude 3,nitro acid. This is dissolved in hot water and the solution concentrated until crystals begin to separate from the hot liquid. It is then allowed to cool slowly and is left four or five hours in a cool place. Most of the 3,nitro-*o*-phthalic acid is thus separated in small hard transparent crystals of a faint yellowish cast, which are further purified by recrystallization from water, the yield then being about 30 per cent. of the theory.

As there is usually some unnitrated phthalic acid in the first precipitate of crude acids, this precipitate was subjected to a second nitration in similar manner. Only a small amount of the crude acid then dissolved in the hot nitrating solution, showing the

[1] *Ber. d. chem. Ges.*, **11**, 393 (1878).

presence of but little phthalic acid. The yield of 3,nitro acid was increased by this second nitration to about 32 per cent. of that theoretically obtainable from phthalic acid.

Method of May,[1] *Edinger*[2] *and Leupold*.[3]—This is quite similar to that of Miller, except that phthalic anhydride is used instead of the acid.

As might be expected from the smaller amount of water present in this reaction, the precipitation of the nitro acids begins much sooner, and after an hour's heating upon the water-bath the mixture in the flask is a nearly solid mass of crystals. This rapid separation of the nitro acids seems to prevent complete nitration, as the yield of pure 3,nitro acid by this process was only about 25 per cent. of the theory, while a renitration raised this figure to nearly 38 per cent. It is quite possible that by the careful addition of water during the first nitration the separation of the nitro acids could be retarded, thereby increasing the yield and obviating the necessity for a second nitration.

In renitrating the crude nitro acids no complications need be feared from formation of dinitrophthalic acids, as Beilstein and Kurbatow[4] have shown that it is exceedingly difficult to further nitrate 3,nitro-*o*-phthalic acid.

The nitration of phthalic acid or of its anhydride thus readily gives good yields of pure 3,nitro-*o*-phthalic acid, and it is the method by which we have prepared the acid for conversion into the derivatives described later.

As thus prepared, 3,nitro-*o*-phthalic acid forms hard transparent prisms, of a very pale yellow color. Its behavior when heated resembles that of the unsubstituted phthalic acid; in an open tube, it decomposes at 207°, or lower, into water and the anhydride, the point at which this decomposition begins depending upon the rapidity of the heating, while in a sealed tube it melts at 222° (corr.). It is quite readily soluble in hot water, much less so in cold; easily soluble in cold acetone; moderately soluble cold, easily hot, in methyl or ethyl alcohols, and ethyl acetate; sparingly soluble in cold isoamyl alcohol, moderately in hot; difficultly soluble in ether; nearly insoluble in petroleum ether, benzene, chloroform, carbon tetrachloride, ethyl nitrate,

[1] Inaug. Dissertation, Freiburg, (1880).
[2] *J. prakt. Chem.*, (2), **53**, 382 (1896).
[3] Inaug. Dissertation, Basle, (1897).
[4] *Loc. cit.*

carbon bisulphide, benzene, and nitrobenzene ; glacial acetic acid, at 26°, takes up 7.5 per cent. (Aguiar,[1] Diehl and Merz).[2] It is much less soluble in all ordinary solvents than the corresponding 4,nitro-*o*-phthalic acid.

Derivatives of 3,Nitro-o-phthalic Acid.

Acid Aniline Salt, $NO_2.C_6H_3\overset{(3)}{<}\begin{matrix}COO.NH_3(C_6H_5)(2)\\COOH\ (1)\end{matrix}$.—The strong tendency of 3,nitro-*o*-phthalic acid to form acid salts with the ammonium bases, rather than neutral salts, was commented upon by Laurent[3] as early as 1842. This peculiarity is still more marked in the case of the aromatic amines, of which no neutral salts with the nitrophthalic acids are known. By adding aniline to the alcoholic solution of 3,nitro-*o*-phthalic acid and then concentrating upon the water-bath, colorless needles of the acid aniline salt separate, melting at 185°–187°, with loss of water and production of the anil. Only the acid salt could be obtained, no matter how large the excess of aniline employed. Several months after the completion of this experiment an article by Graebe and Buenzod[4] appeared, in which they record similar results.

As the carboxyl adjacent to the nitro group is the stronger of the two, it seems most likely that this acid salt has the formula given above.

Acid o-Toluidine Salt, $NO_2.C_6H_3\overset{(3)}{<}\begin{matrix}COO.NH_3(C_6H_4.CH_3)(2)\\COOH\ (1)\end{matrix}$.—Prepared in a similar manner, this acid salt forms fine white needles melting at 181°, a few degrees above which point it breaks up into water and the *o*-tolil. Its aqueous solution is acid to carbonates and to litmus.

Acid Ethyl Ester, $NO_2.C_6H_3<\begin{matrix}COO.C_2H_5(2)\\COOH(1)\end{matrix}$.—3,Nitrophthalic anhydride was dissolved in absolute alcohol in a flask carrying a reflux condenser, and the solution heated for five hours upon the water-bath. Upon distilling off the alcohol, a yellow oil remained, which was dissolved in strong sodium carbonate solution and the mixture extracted with ether, to remove any neutral

[1] *Ber. d. chem. Ges.*, **5**, 899 (1872).
[2] *Ibid.*, **11**, 1667 (1878).
[3] *Ann. Chem.* (Liebig), **41**, 110 (1842).
[4] *Ber. d. chem. Ges.*, **32**, 1992 (1899).

ester (none was found). The addition of hydrochloric acid to the sodium carbonate solution caused the separation of a white crystalline precipitate, melting at 157°, soluble in alcohol or ether, but insoluble in cold water. Its solutions decompose carbonates and are acid to litmus. The substance was dissolved in alcohol and titrated with tenth-normal sodium hydroxide solution. 0.807 gram of the substance took 33.3 cc. of the tenth-normal sodium hydroxide; theory requires 33.7 cc. The silver salt forms nearly colorless crystals.

The isomeric acid ethyl ester, with the ester group meta to the nitro, and melting at 110°, was first obtained (in the impure state) by Faust,[1] and, subsequently described by Baeyer,[2] Miller,[3] Nerking,[4] and Edinger.[5]

Anhydride, $NO_2.C_6H_3\begin{matrix}CO\\ \diagup\diagdown O\\ CO\end{matrix}$.—Laurent,[6] Faust,[7] and Miller[8] all state that the anhydride is formed by the action of heat upon the acid. Recently, however, Lipschitz[9] reported that by careful heating of the acid at 220°, even in a stream of carbon dioxide, he obtained only a brown melt containing decomposition products with the odor of nitrogen dioxide and benzaldehyde. Our experience has been more in accord with that of the earlier investigators. The 3,nitro acid, in a small flask, was heated in an oil-bath at 235°–240° until water vapor ceased to be given off (six to eight hours' heating necessary). On cooling, a yellow crystalline solid appeared, which was nearly pure anhydride, and, after a single crystallization from glacial acetic acid or acetone, formed colorless needles melting sharply at 163°. If there should be any indication of unchanged acid in the product, it may be crystallized from acetyl chloride, which likewise converts the acid to the anhydride.[10] The anhydride is easily soluble in acetyl chloride or hot glacial acetic acid, moderately in acetone or hot alcohol, and very difficultly soluble in benzene.

[1] *Ann. Chem.* (Liebig), **160**, 57 (1871).
[2] *Ber. d. chem. Ges.*, **10**, 125, 1079 (1877).
[3] *Ann. Chem.* (Liebig), **208**, 223 (1881).
[4] Inaug. Dissertation, Heidelberg, (1896).
[5] *J. prakt. Chem.*, (2), **53**, 382 (1896).
[6] *Ann. Chem.* (Liebig), **41**, 110 (1842).
[7] *Ztschr. Chem.* 1869, 108; *Ann. Chem.* (Liebig), **160**, 57 (1871).
[8] *Ann. Chem.* (Liebig), **208**, 223 (1881).
[9] *Monatsh. Chem.*, **21**, 787 (1900).
[10] Leupold: *Loc. cit.*; Lipschitz: *Loc. cit.*

Imide, $NO_2.C_6H_3\begin{matrix}CO\\CO\end{matrix}NH$.—Laurent[1] states that when the ammonium salt of 3,nitro-*o*-phthalic acid is distilled the free acid is regenerated and no imide is formed; also, that when the anhydride is treated with dry ammonia gas a new compound is obtained, but he gives none of the properties of this "new compound." We have, therefore, prepared this imide by the action of heat upon the acid ammonium salt. The salt begins to decompose at about 225°, and the heating is continued until no more water vapor is evolved and the melt remains in quiet fusion. On cooling, a yellow crystalline solid is obtained, easily soluble in acetone, moderately in hot alcohol or hot glacial acetic acid, and very difficultly in water. It crystallizes from alcohol in pale yellow lustrous needles melting at 215°–216°.

I. 0.1513 gram substance gave 20 cc. nitrogen at 22° and 753 mm.
II. 0.1694 gram substance gave 22.1 cc. nitrogen at 22° and 751.5 mm.

	Calculated for $C_8H_4O_4N_2$.	Found. I.	II.
Nitrogen.....	14.62	14.82	14.51

By dissolving the imide in a mixture of alcohol and acetone and adding exactly one molecule of potassium hydroxide dissolved in alcohol, a white crystalline precipitate of the potassium salt of the imide results.

Amide, $NO_2.C_6H_3\begin{matrix}CO.NH_2\\CO.NH_2\end{matrix}$.—Strong ammonium hydroxide is added to the imide and the mixture warmed slightly. The lustrous flaky crystals of the imide gradually disappear and in their place a sandy crystalline precipitate appears, the reaction being complete at the end of about one hour. Dried to constant weight over sulphuric acid *in vacuo*, the following analytical results were obtained from the substance:

0.1452 gram substance gave 26.1 cc. nitrogen at 22° and 758 mm.

	Calculated for $C_8H_7O_4N_3$.	Found.
Nitrogen.....	20.1	20.3

When heated in an open tube, the amide melts at 200°–201° with evolution of ammonia, remelting, after cooling, at 215°, the melting-point of the imide.

[1] *Loc. cit.*

Amidic Acid, $NO_2.C_6H_3\begin{cases}(3)\\CO.NH_2\ (2)\\COOH\ (1)\end{cases}$.—Baryta water is added to the imide and the mixture heated for an hour at 80°, and then allowed to stand for twenty-four hours at the ordinary temperature. Upon acidifying with sulphuric acid, the barium sulphate precipitate carries down with it some of the amic acid, which may be recovered by extraction with cold strong alcohol. Concentration of the filtrate from the barium sulphate precipitation, or of the alcoholic extracts, yields white needles of the amidic acid. This concentration must be carried out cold, by blowing a stream of dry air through the liquid, as hot concentration appears to destroy the amic acid, probably causing hydration. The crystals of amic acid were washed with ether, and dried *in vacuo* over sulphuric acid. They melt at 156°, with evolution of water, and, after solidifying, remelt at 213°, showing the production of the imide. The amidic acid is but sparingly soluble in cold water, easily in alcohol, and apparently insoluble in ether. Its solutions are acid to litmus and decompose carbonates.

0.1509 gram substance gave 17.6 cc. nitrogen at 22° and 755 mm.

	Calculated for $C_8H_6O_5N_2$.	Found.
Nitrogen.....	13.3	13.13

Ethylimide, $NO_2.C_6H_3\begin{cases}CO\\CO\end{cases}N.C_2H_5$.—When the acid ethylamine salt is heated at 125°–165° for some time there results a greenish crystalline solid, sparingly soluble in hot water, but easily in hot alcohol. From the latter solvent it crystallizes in long lustrous needles of yellowish cast, melting at 105°.

0.1747 gram substance gave 20.4 cc. nitrogen at 27.5° and 760 mm.

	Calculated for $C_{10}H_8O_4N_2$.	Found.
Nitrogen.....	12.7	12.85

Attempts to prepare the same compound by the action of ethyl iodide upon the potassium salt of the imide, in sealed tubes, all resulted unsatisfactorily.

Anil, $NO_2.C_6H_3\begin{cases}CO\\CO\end{cases}N.C_6H_5$.—Aniline and 3,nitro-*o*-phthalic anhydride are heated together at about 190°, or, better, the acid aniline salt is carefully heated. In the latter case, an amber colored solid is obtained, soluble in acetone, difficultly soluble in

cold alcohol, moderately in hot. Crystallized from a mixture of alcohol and acetone, it forms yellowish needles, melting at 136°–137°. Graebe and Buenzod,[1] whose article, as already explained, appeared subsequent to the completion of this part of the work, give 134° as the melting-point of the anil.

Anilic Acid, $NO_2.C_6H_3\begin{cases}(3)\\ \\ \\ \end{cases}\begin{matrix}CO.NH(C_6H_5)\ (2)\\ \\ COOH\ (1)\end{matrix}$.—This compound may be prepared from the anil in a manner entirely analogous to that for the preparation of the amic acid from the imide, except that when the baryta solution is acidified by sulphuric acid most of the anilic acid separates with the barium sulphate as a flocculent precipitate, which must be dissolved out by cold alcohol, and the solution concentrated cold as already described. Pale yellow needles are thus obtained, which can be washed with ether and dried. These needles melt at 180°, and, after resolidifying, the melting-point sinks to 135°, showing conversion of the anilic acid to the anil (m. p. 136°). The anilic acid is easily soluble in alcohol, difficultly in cold water, and apparently insoluble in ether. Its solutions are acid to litmus but do not seem to decompose carbonates.

0.1962 gram substance gave 17.4 cc. nitrogen at 23° and 758 mm.

	Calculated for $C_{14}H_{10}O_5N_2$.	Found.
Nitrogen	9.8	9.96

o-Nitranil, $NO_2.C_6H_3\begin{cases}CO\\ \\ CO\end{cases}N—C_6H_4—NO_2(o\text{-})$.—When the acid *o*-nitraniline salt is heated it begins to decompose at 150° with loss of water, and at 200° the last portions of water are removed. The yellowish mass resulting, when crystallized from a mixture of alcohol and acetone, gives yellow crystals of the *o*-nitranil, melting at 167°.

0.1619 gram substance gave 20 cc. nitrogen at 25° and 759 mm.

	Calculated for $C_{14}H_7O_6N_3$.	Found.
Nitrogen	13.4	13.7

m-Nitranil is prepared by heating the acid *m*-nitraniline salt at 170°–200°. The product is less soluble in alcohol or acetone than the corresponding ortho compound, and, when crystallized from a mixture of these solvents, forms pale brown, microscopic crystals, melting at 219°.

[1] *Loc. cit.*

p-Nitranil.—The acid *p*-nitraniline salt was heated at 200°–250° until water ceased to be evolved. The brown crystalline mass resulting was purified by crystallization from acetone, in which it was only moderately soluble, small yellow crystals of the *p*-nitranil being thus obtained, of a melting-point of 249°.

o-Tolil, $NO_2.C_6H_3\begin{matrix}CO\\ \diagup\\ \diagdown\\ CO\end{matrix}N—C_6H_4.CH_3(o\text{-})$.—By heating the acid *o*-toluidine salt at 160°–190°, and crystallizing the product from a mixture of alcohol and acetone, pale yellow needles of the *o*-tolil result, melting at 145°. These are easily soluble in acetone, and only sparingly in alcohol.

m-Tolil is prepared in a similar manner, the acid *m*-toluidine salt losing its water at about the same temperature as the ortho compound. From a mixture of alcohol and acetone, it crystallizes in long yellow needles, melting at 129°.

p-Tolil.—Equal molecules of *p*-toluidine and 3,nitro-*o*-phthalic anhydride were heated together at 170°–180° until the evolution of water ceased. The *p*-tolil thus obtained crystallizes from a mixture of alcohol and acetone in pale yellow needles (m. p. 154°).

0.2003 gram substance gave 18.3 cc. nitrogen at 23° and 752 mm.

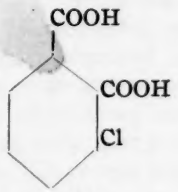
	Calculated for $C_{15}H_{10}O_4N_2$.	Found.
Nitrogen.....	9.93	10.17

Hydrazide, $NO_2.C_6H_3\begin{matrix}CO—NH\\ \diagup\ \ |\\ \diagdown\ \ |\\ CO—NH\end{matrix}$ or $NO_2.C_6H_3\begin{matrix}CO\\ \diagup\\ \diagdown\\ CO\end{matrix}N.NH_2$.

—3,Nitro-*o*-phthalic acid was dissolved in alcohol, one molecule of hydrazine hydroxide (in 50 per cent. aqueous solution) added, and the solution evaporated to dryness. The residue was then carefully heated in an oil-bath. At 150° the evolution of water began and continued until the temperature reached 250°. Even at this latter temperature the material did not melt, but remained a pale brown, porous solid. It dissolved readily in a warm sodium carbonate solution, with effervescence, forming a yellowish red liquid. Acidification with hydrochloric acid caused the precipitation of a yellow powder, which crystallized from glacial acetic acid in pale yellow, microscopic crystals, melting with decomposition at about 320°. These crystals are likewise decomposed by caustic alkali.

0.1510 gram substance gave 27.4 cc. nitrogen at 24° and 761 mm.

	Calculated for $C_8H_5O_4N_3$.	Found.
Nitrogen	20.3	20.36



3,Chlor-o-phthalic Acid.

Anhydride, $Cl.C_6H_3\begin{matrix}CO\\CO\end{matrix}O$.—Ten grams of 3,nitro-*o*-phthalic anhydride and 11 grams phosphorus pentachloride were heated together in a sealed tube for six hours at 175°. From the contents of the tube pale yellow crystals were separated, which, after recrystallization from a mixture of benzene and naphtha, formed nearly colorless needles, melting at 122°, corresponding to that recorded by Krüger[1] for 3,chlor-*o*-phthalic anhydride.

0.1763 gram substance gave 0.1415 gram silver chloride.

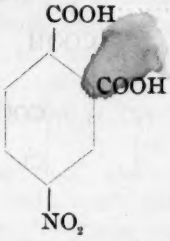
	Calculated for $C_8H_5O_3Cl$.	Found.
Chlorine	19.4	19.8

Acid, $Cl.C_6H_3\begin{matrix}COOH\\COOH\end{matrix}$.—By boiling the anhydride obtained above for several hours with dilute hydrochloric acid, the corresponding chlorphthalic acid was obtained. This crystallized from water in colorless needles (m. p. 186°). Guareschi[2] found the melting-point of 3,chlor-*o*-phthalic acid to be 184°.

Imide, $Cl.C_6H_3\begin{matrix}CO\\CO\end{matrix}NH$.—The 3,chlor-*o*-phthalic anhydride was dissolved in strong ammonium hydroxide, the solution evaporated to dryness, and the residue carefully heated. A sublimate of white needles resulted. In an open tube, these needles sublime before melting; in a closed tube they melt at 118°–120°. The substance appears to be the 3,chlorphthalimide, which has

[1] *Ber. d. chem. Ges.*, **18**, 1759 (1885).
[2] *Gaz. chim. ital.*, **17**, 120.

not been previously described, but not sufficient of the substance was prepared for an analysis.



β, OR 4,NITRO-*o*-PHTHALIC ACID.

Preparation of the Acid.

Method of Miller.[1]—As has been stated, the action of a mixture of concentrated sulphuric acid and fuming nitric acid upon phthalic acid produces about equal amounts of the two nitro-*o*-phthalic acids. Of these, the 3,nitro acid is readily separated in the pure state by virtue of its sparing solubility in water. The isolation of the 4,nitro acid, however, is a matter of much greater difficulty, not only on account of its great solubility, but also from the fact that the picric acid present tends to follow it through and to combine with it or its salts in crystallization, so that even by the recrystallization of its difficultly soluble barium salt only about 15 per cent. pure 4,nitro acid can be recovered from the original precipitate of crude acids. A much better method of separation depends upon the fact that when a mixture of these two acids is esterified by the action of hydrochloric acid gas upon their alcoholic solution the 3,nitro acid yields mainly the acid ester, while the 4,nitro acid is converted into the neutral ester. By treating the product of this esterification with strong sodium carbonate solution, the acid ester (together with picric acid) is dissolved out, leaving the neutral ester of the 4,nitro acid as an insoluble oil.

In applying this process, we usually crystallized out as much of the 3,nitro acid as possible from the crude nitro acids, then evaporated the mother-liquors to dryness, dissolved the residue in absolute alcohol and esterified with dry hydrochloric acid gas. Upon the addition of water, then, the esters separate as an oily layer, which is washed repeatedly with strong sodium carbonate

[1] *Ber. d. chem. Ges.*, **11**, 393 (1878); *Ann. Chem.* (Liebig), **208**, 223 (1881).

solution. The neutral ester of the 4,nitro acid is thereby left as an oil, which gradually solidifies, and is purified by crystallization from ether and then from alcohol, forming large pale yellow plates, melting at 34°–35°. From this neutral ester the free acid may be prepared by saponifying with alcoholic potassium hydroxide, dissolving the precipitated potassium salt in water, acidifying the solution with hydrochloric acid and extracting with ether. Evaporation of the ether leaves the 4,nitro-*o*-phthalic acid as a crystalline crust, melting at 162°.

Although the yield by this process is good, the purification of the neutral ester is rather troublesome, as it is apt to contain small amounts of the neutral esters of 3,nitro-*o*-phthalic acid and of phthalic acid itself, the presence of the latter preventing the solidification of the oily ester.

Preparation of the Acid from p-Nitrophthalide.—Hoenig[1] was the first to prepare the 4,nitro-*o*-phthalic acid from the nitrophthalide (m. p. 141°) by oxidation. He found the best oxidizing agents to be a mixture of glacial acetic acid and chromic anhydride, or, better, dilute nitric acid in a sealed tube.

Oxidation by glacial acetic acid and chromic anhydride is far from satisfactory, and much the same may be said concerning the use of dilute nitric acid. The latter method is also open to the objection that it is not convenient for the preparation of large amounts of material.

Hoenig[2] further states that oxidation of the nitrophthalide by means of alkaline potassium permanganate gave no result. We have found, on the contrary, that this is much the best oxidizing agent for the purpose, 90 per cent. of the theoretical yield of 4,nitro-*o*-phthalic acid being thereby readily and rapidly obtained, the ease and rapidity of the method rendering it by far the best method of preparing the 4,nitro-*o*-phthalic acid pure and absolutely free from its isomer.

The oxidation is carried out as follows: *p*-nitrophthalide is dissolved in dilute alkali, the solution placed in a large evaporating dish on the water-bath, and potassium permanganate solution added gradually until the oxidation is completed. Excess of permanganate is then destroyed by the addition of a little alcohol, the manganese dioxide filtered off and the precipitate washed

[1] *Ber. d. chem. Ges.*, **18**, 3447 (1885).
[2] *Loc. cit.*

once or twice with hot water. The filtrate and washings are combined, concentrated to about 150 cc., acidified with hydrochloric acid, and repeatedly extracted with ether. The ether extracts are combined, dried with calcium chloride, and the ether evaporated, leaving the pure 4,nitro-*o*-phthalic acid as a pale yellow crystalline mass (m. p. 163°).

The 4,nitro acid loses water a few degrees above its melting-point, being thereby changed to the anhydride. The acid is easily soluble in water, methyl or ethyl alcohols, and acetone; moderately in ether or ethyl acetate; sparingly in cold isoamyl alcohol or glacial acetic acid, easily in hot; apparently insoluble in petroleum ether, benzine, chloroform, carbon tetrachloride, ethyl nitrate, carbon disulphide, benzene, and cold nitrobenzene; moderately soluble in hot nitrobenzene.

Derivatives of 4,Nitro-o-phthalic Acid.

Acid Aniline Salt, $NO_2.C_6H_3\begin{cases}COO.NH_3(C_6H_5)\ (1)\\ COOH\ (2)\end{cases}$ (4).—Like the 3,nitro acid, the 4,nitro-*o*-phthalic acid appears incapable of forming neutral salts with the aromatic amines. As prepared by us, this acid aniline salt melts at 181°–182° with production of the anil. It has also been described by Graebe and Buenzod.[1] It seems probable that in these acid salts the para carboxyl carries the base.

Acid Ethyl Ester, $NO_2.C_6H_3\begin{cases}COO.C_2H_5\\ COOH\end{cases}$.—Miller,[2] by evaporating an absolute alcohol solution of the 4,nitro-*o*-phthalic anhydride, reports the production of an acid ester different from the ordinary one (m. p. 127°–128°), but does not describe any of its properties. We have, therefore, repeated the experiment:

4,nitro-*o*-phthalic anhydride was dissolved in absolute alcohol in a flask fitted with a reflux condenser, the solution boiled for eight hours on the water-bath, and the alcohol then distilled off. A reddish brown oil remained. This oil dissolved, with effervescence, in sodium carbonate solution. The sodium carbonate solution was then extracted with ether, to remove any neutral ester which might have formed, the residual alkaline liquid acidified

[1] *Loc. cit.*

[2] *Ann. Chem.* (Liebig), **208**, 223 (1881).

with hydrochloric acid, and the turbid acid solution again subjected to extraction with ether. This ether extract was dried with calcium chloride and the ether evaporated, leaving a yellow oil, which, after standing about eight hours over sulphuric acid in vacuo, solidified to a pale yellow, amorphous mass, melting at 141°–150°. Recrystallization failed to yield a substance with any sharper melting-point. The acid ethyl ester, produced by the action of dry hydrochloric acid gas upon the alcoholic solution of the 4,nitro acid, melts sharply at 127°–128°. The acid ethyl ester described above appears, therefore, to be an isomer (although probably impure).

This result is rather at variance with the investigations of Wegscheider and Lipschitz[1] in preparing the methyl esters of 4,nitro-*o*-phthalic acid, as they obtained the same acid ester by the action of methyl alcohol upon the anhydride as by the action of hydrochloric acid gas upon the methyl alcohol solution of the free acid.

Anhydride, $NO_2.C_6H_3\begin{matrix}CO\\CO\end{matrix}O$.—By heating the 4,nitro acid at 165° until no more water is evolved and then cooling, a sticky, yellow mass remains. Miller[2] heated this mass to 200° and sublimed the anhydride by passing a current of dry air through the melt. We have found it more convenient to dissolve this sticky mass in hot acetyl chloride and evaporate the solution to crystals. Pale yellow needles of the anhydride are thus obtained, melting sharply at 114°, which are easily soluble in acetyl chloride, hot glacial acetic acid or hot alcohol, and but sparingly in hot benzene.

Leupold[3] prepared this anhydride by heating the acid in sealed tubes with acetyl chloride.

Imide, $NO_2.C_6H_3\begin{matrix}CO\\CO\end{matrix}NH$, is prepared by the action of heat upon the acid ammonium salt, in similar manner to the preparation of the imide of the 3,nitro acid. It crystallizes from a mixture of alcohol and acetone in pale yellowish brown flakes, melting at 197°. It is easily soluble in hot acetone, sparingly in hot alcohol or hot water.

[1] *Monatsh. Chem.*, **21**, 787 (1900).
[2] *Ann. Chem.* (Liebig), **208**, 223 (1881).
[3] Inaug. Dissertation, Basle, 1897.

I. 0.1804 gram substance gave 24 cc. nitrogen at 23° and 755 mm.
II. 0.1494 gram substance gave 19.9 cc. nitrogen at 22° and 756 mm.

	Calculated for $C_8H_4O_4N_2$.	Found. I.	Found. II.
Nitrogen	14.62	14.96	15.00

By dissolving the imide in a mixture of alcohol and acetone and adding one molecule of alcoholic potassium hydroxide, the potassium salt of the imide separates as a white precipitate, slightly soluble in cold strong alcohol easily soluble in water.

Amide, $NO_2.C_6H_3\begin{cases}CO.NH_2\\CO.NH_2\end{cases}$.—The imide was mixed with strong ammonium hydroxide and dissolved by gentle warming. After standing for an hour at the temperature of the room, a heavy white crystalline precipitate appeared. This precipitate was filtered out, washed with a little cold water, and dried finally *in vacuo* over sulphuric acid. It then melted at 200° with evolution of ammonia, and when remelted, after solidifying, showed the melting-point of the imide (197°).

0.1430 gram substance gave 25.9 cc. nitrogen at 22.5° and 755 mm.

	Calculated for $C_8H_7O_4N_3$.	Found.
Nitrogen	20.1	20.3

Amic Acid.—Attempts to prepare the aminic acid of the 4,nitro-*o*-phthalic acid by the same process that yielded the aminic acid of the 3,nitro-*o*-phthalic acid have so far been entirely unsatisfactory.

Ethylimide, $NO_2.C_6H_3\begin{cases}CO\\CO\end{cases}N.C_2H_5$, is prepared by the action of heat upon the acid ethylamine salt, or by heating the potassium salt of the imide in a sealed tube with ethyl iodide. Pale yellow scales (m. p. 111°–112°) are slightly soluble in hot water, readily in alcohol or ether.

0.1805 gram substance gave 20.6 cc. nitrogen at 23° and 758 mm.

	Calculated for $C_{10}H_8O_4N_2$.	Found.
Nitrogen	12.7	12.83

Anil, $NO_2.C_6H_3\begin{cases}CO\\CO\end{cases}N.C_6H_5$, results when the acid aniline salt is heated above its melting-point. It crystallizes from a mixture of alcohol and acetone in yellow needles, melting at

194°. It is moderately soluble in acetone, sparingly in alcohol. Graebe and Buenzod[1] give its melting-point as 192°.

Anilic Acid, $NO_2.C_6H_3\langle^{CO.NH(C_6H_5)}_{COOH}$, is prepared by the action of baryta water upon the anil. When the baryta solution is acidified with sulphuric acid the anilic acid precipitates with the barium sulphate, and must be extracted from it with cold alcohol. It forms pale yellow crystals, melting at 181° with formation of the anil. It is easily soluble in cold alcohol, nearly insoluble in ether, and apparently totally insoluble in cold water. Its solutions are acid to litmus but do not decompose carbonates.

0.1955 gram substance gave 17.2 cc. nitrogen at 25° and 761 mm.

	Calculated for $C_{14}H_{10}O_5N_2$.	Found.
Nitrogen.....	9.8	9.83

o-Nitranil, $NO_2.C_6H_3\langle^{CO}_{CO}\rangle N.C_6H_4.NO_2(o\text{-})$, is prepared by the action of heat upon the acid *o*-nitraniline salt. It crystallizes from nitrobenzene in pale yellow needles (m. p. 233°), difficultly soluble in acetone, very slightly in alcohol, and readily in hot nitrobenzene.

m-Nitranil is prepared in a similar manner from the acid *m*-nitraniline salt. It crystallizes from nitrobenzene in opaque yellow needles (m. p. 243°). It is sparingly soluble in alcohol or acetone, but readily in hot nitrobenzene.

p-Nitranil is prepared in a similar manner, crystallizes from nitrobenzene in small yellow crystals, melting at 251°–253°, difficultly soluble in acetone, apparently insoluble in alcohol, but easily soluble in hot nitrobenzene.

o-Tolil, $NO_2.C_6H_3\langle^{CO}_{CO}\rangle N.C_6H_4.CH_3$ (*o*-), is obtained by the action of heat upon the acid *o*-toluidine salt, and forms a brownish crystalline powder (m. p. 160°). It is very slightly soluble in alcohol, moderately in acetone.

m-Tolil is prepared in a similar manner from the acid *m*-toluidine salt. Pale brownish crystals (from nitrobenzene, m. p. 197°) are practically insoluble in alcohol, difficultly soluble in acetone, easily in hot nitrobenzene.

[1] *Loc. cit.*

p-Tolil is produced by heating together *p*-toluidine and 4,nitro-*o*-phthalic anhydride at 180°–190°. It crystallizes from a mixture of alcohol and acetone in yellow pearly flakes, melting at 165°, slightly soluble in alcohol, readily in acetone.

0.1935 gram substance gave 17.5 cc. nitrogen at 22.5° and 751 mm.

	Calculated for $C_{15}H_{10}O_4N_2$.	Found.
Nitrogen	9.93	10.14

p-Tolilic Acid, $NO_2.C_6H_3\begin{cases}CO.NH(C_6H_5.\overset{(p)}{C}H_3)\\ COOH\end{cases}$. — *p*-Tolil is heated for fifteen minutes on the water-bath with baryta water, and the mixture then allowed to stand twenty-four hours at the room temperature. The flaky crystals of tolil are gradually replaced by long yellow needles of the barium salt of the tolilic acid. Upon the addition of sulphuric acid, the free tolilic acid precipitates with the barium sulphate and may be extracted from it by strong alcohol. On cold evaporation of the alcohol, the tolilic acid remains in white needles, melting at 172° (with formation of the tolil). The tolilic acid is insoluble in ether or cold water, does not decompose carbonates, but reacts acid to litmus.

Hydrazide, $NO_2.C_6H_3\begin{cases}CO—NH\\ \quad\quad|\\ CO—NH\end{cases}$ or $NO_2.C_6H_3\begin{cases}CO\\ \\ CO\end{cases}N.NH_2$. —A solution of 4,nitro-*o*-phthalic anhydride was treated with one molecule of hydrazine hydrate (in 50 per cent. aqueous solution), and the mixture warmed for several hours. No precipitate formed, but, upon evaporation, a red oil remained, which changed to a yellowish brown precipitate when water was added. This precipitate was boiled down repeatedly with water, and finally washed with water, alcohol, and ether. In warm sodium carbonate solution it dissolved with effervescence, and reprecipitated in pale yellow flocks when the solution was acidified. Recrystallized from water, it forms a microcrystalline powder.

0.1503 gram substance gave 27.4 cc. nitrogen at 24° and 750 mm.

	Calculated for $C_8H_5O_4N_3$.	Found.
Nitrogen	20.3	20.16

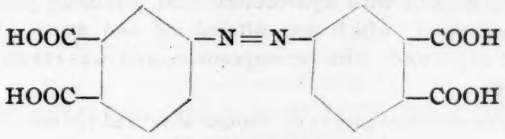
4,Nitro-*o*-phthalic acid was dissolved in water, one molecule of hydrazine hydrate added, the liquid evaporated to dryness, and the residue carefully heated. At 150° the mass began to soften

and evolve water, but the reaction did not appear completed until the temperature had reached about 250°. Even at this temperature the mass refused to melt, remaining hard and porous. It was purified by solution in sodium carbonate, reprecipitation, etc., as in the foregoing case, and yielded a similar product.

0.1733 gram substance gave 32 cc. nitrogen at 22° and 743 mm.

	Calculated for $C_8H_5O_4N_3$.	Found.
Nitrogen	20.3	20.45

The hydrazide forms small yellow crystals, slightly soluble in water or alcohol, difficultly soluble in glacial acetic acid. When heated to 270° it gives a white sublimate, then darkens at 280°, but does not melt even at 300°. Heated with acetic anhydride for several hours, no definite acetyl derivatives could be obtained.



4,4′,AZOPHTHALIC ACID.

Preparation from 4,Nitro-o-phthalic Acid.—4,Nitro-*o*-phthalic acid was dissolved in dilute caustic soda, and the solution reduced by the gradual addition of 2 per cent. sodium amalgam. After the requisite amount of amalgam had been added, the mixture was heated for an hour upon the water-bath, the red alkaline solution decanted from the mercury, concentrated, and acidified with hydrochloric acid. A yellowish red precipitate appeared, which was filtered off, dried, and crystallized from water. It then formed a salmon-colored crystalline powder, moderately soluble in hot water, slightly in alcohol or glacial acetic acid, and insoluble in ether. It refused to melt at 360°. Its aqueous solution was acid to litmus and decomposed carbonates.

0.2046 gram substance gave 14 cc. nitrogen at 23° and 762 mm.

	Calculated for $C_{16}H_{10}O_8N_2$.	Found.
Nitrogen	7.8	7.73

The compound was unchanged by boiling with glacial acetic acid and sodium nitrite, showing the absence of hydrazo combinations.

The silver salt was prepared by adding a solution of argentic nitrate to the solution of the neutral ammonium salt. It separated as a red precipitate, insoluble in hot water, and when dried to

constant weight at 110°, appeared as a heavy red crystalline powder.

0.2039 gram substance yielded, upon ignition, 0.1085 gram silver.

	Calculated for $C_{16}H_6O_8N_2Ag_4$.	Found.
Silver	54.9	53.2

This low result is accounted for by the fact that the silver salt explodes when heated to a certain point, thus rendering the securing of accurate results a matter of considerable difficulty.

Preparation from Azophthalide.—An alkaline solution of 5,5′,-azophthalide was oxidized by potassium permanganate in the manner already described for the conversion of nitrophthalide into 4,nitro-*o*-phthalic acid. By acidifying the filtrate from the manganese dioxide with hydrochloric acid, a reddish yellow precipitate separated, which was filtered off and dried. It then melted at 285°–300°, with decomposition, and was crystalline in appearance.

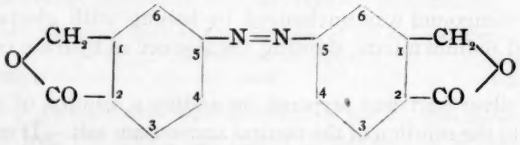
0.1946 gram substance gave 13 cc. nitrogen at 22° and 752 mm.

	Calculated for $C_{16}H_{10}O_8N_2$.	Found.
Nitrogen	7.8	7.8

The silver salt formed a heavy red crystalline powder, somewhat soluble in hot water, and exploded when heated.

It will be noted that the azophthalic acid obtained by this process melts, with decomposition, at a temperature somewhat below 300°, and gives a silver salt which is partly soluble in hot water, while that obtained by reduction of 4,nitrophthalic acid does not melt at 360°, and its silver salt appears to be insoluble in hot water. The cause of this difference has not as yet been determined. It will be made the subject of further investigation.

The corresponding 3,3′,azophthalic acid has been prepared by Claus and May[1] by the reduction of the 3,nitro-*o*-phthalic acid with sodium amalgam, and forms golden yellow needles, decomposing at 220°–250°.



[1] *Ber. d. chem. Ges.*, **11**, 762 (1878); **14**, 1330 (1881).

5,5', Azophthalide.

This was obtained by the action of a 2 per cent. sodium amalgam upon the dilute alkaline solution of *p*-nitrophthalide. Hydrochloric acid is added to the resultant alkaline solution, and the red precipitate obtained is filtered off and dried. From dilute alcohol, it forms small red crystals, melting with decomposition at 260°–280°. It is sparingly soluble in hot water, moderately in hot alcohol or glacial acetic acid.

0.2000 gram substance gave 17.6 cc. nitrogen at 26° and 756 mm.

	Calculated for $C_{16}H_{10}O_4N_2$.	Found.
Nitrogen	9.5	9.6

This work is being continued and other papers upon the subject will be published.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY,
July 1, 1901.

ON THE EXISTENCE OF A NEW ELEMENT ASSOCIATED WITH THORIUM.[1]

By CHARLES BASKERVILLE.

Received August 15, 1901.

ALMOST five years ago I attempted to separate thorium quantitatively from a neutral chloride solution by saturation with sulphur dioxide and boiling. As may be recalled, this was merely an application of the method formerly made known by me and used in the separation of zirconium[2] and titanium.[3] The separation of thorium by this means was not quantitative. On resolution of the precipitated portion in hydrochloric acid and exact neutralization with ammonium hydroxide and treatment again with sulphur dioxide, almost complete precipitation resulted, showing that the initial partial precipitation was not altogether due to imperfect action of the precipitant or the solubility of the basic thorium sulphite[4] in the neutral menstruum. This was verified by many repetitions of the process using thorium chloride solutions of different strengths and varying amounts of ammonium chloride.

[1] Presented at the Denver meeting of the American Chemical Society.

[2] *Chem. News*, **70**, 57 (1894); This Journal, **16**, 475 (1894).

[3] This Journal, **16**, 437 (1894).

[4] These basic sulphites are being investigated at present. It may be well to state that in addition to a flocculent basic sulphite there has been obtained a gelatinous compound, or hydrogele, similar in appearance to the zirconium sulphite described by Venable and Baskerville, this Journal, **17**, 448 (1895).

These solutions were first made upon fairly pure thorium salts prepared by me from oxides obtained from analyses of many monazite sands for the North Carolina Geological Survey.[1] As this conduct was unexpected and not in keeping with the observed reactions of the group, the experiments were repeated with thorium compounds obtained from different sources with like results. I was favored with several grams of thorium sulphate prepared by Professor Dunnington, of Virginia, from monazite sand found in Amelia County (Va). Prof. Dennis, of Cornell, kindly gave me 3.5 grams thorium nitrate (99.6 per cent. pure). The hydroxide from which it had been prepared was separated by means of potassium hydronitrate.[2] I worked up about 5,000 liters of thorium sulphate solution obtained from Carolina monazite kindly collected by the late Mr. H. B. C. Nitze, assistant state geologist. The procedure followed need not be detailed here, as it will appear in a subsequent and more extended communication. Finally, Dr. Waldron Shapleigh generously gave me 2 kilograms of the purest thorium oxalate to be had at the Auer Welsbach works. My thanks are due these gentlemen for their kindness.[3]

The purest thorium compounds were repurified by the following procedure: The sulphate was taken up in cold water, treated with sodium sulphate and allowed to stand from twelve to twenty-four hours to insure separation of the remaining cerium salts, the percentage of which was quite small. The liquid was filtered

[1] Bulletin 9, "Monazite and Monazite Deposits in N. C.," 1895.

[2] This Journal, **18**, 947 (1896).

[3] While in the midst of repurifying the compounds from such varied sources and desiring to leave no stone unturned in the investigation, during the fall of last year I wrote Prof. Bohuslav Brauner, of Prague, of my observations and requested a small amount of the purified thorium compound used by him in his excellent work on the atomic weight of that element (*J. Chem. Soc.*, London (Trans.), **73**, 951 (1898)). Very likely the letter went astray as I have received no reply. I was surprised, therefore, to observe in the proceedings of the London Chemical Society (April 10, 1901), an article by him on "Contributions to the Chemistry of Thorium," in which he gives good evidence of the complexity of thorium, dividing that element into Thα and Thβ. Immediately at my first opportunity (April 23), at the spring meeting of the N. C. Section of the American Chemical Society, I made public mention of my work, which had been discussed often in private with others. Brauner's results were obtained by hydrolysis of the heptahydrated thorium tetrammonium oxalate. This communication contains in part the results of my experiments reported then and some observations made since. As soon as the unexpected properties were noted almost five years ago, I indicated the differences by terming one Th and the other Th(X). It is deemed well to make this explanation in presenting a preliminary paper on incomplete work, as it was done independently and the problem was attacked in a different way. Results have been obtained which corroborate Brauner's work. It may also be stated that large quantities of the materials are being worked up and the work will be pushed to a finality.

and the hydroxide precipitated in tall cylinders by a large excess of chemically pure sodium nitrite. This precipitate was washed by decantation from six to ten times, using 20 volumes (to 1 of precipitate) of distilled water each time. To remove the last of the sodium salts and other soluble impurities the precipitate was then dissolved in hydrochloric acid reprecipitated by slight excess of ammonium hydroxide and washed by decantation at least ten times, using 20 volumes of distilled water.

I. VARIATION IN THE SPECIFIC GRAVITY OF THE OXIDE.

The determination of the specific gravity of the oxides affords a rapid and excellent means of judging the rate of fractionation and in a measure the purity of the rare earths. This method has been especially urged independently by Muthmann and Bohm[1] as having time advantages over the necessarily long and often tedious equivalent determinations. Brauner also uses the method. The oxide obtained by prolonged ignition with the blast of the purified hydroxide obtained above had a specific gravity of 10.1 corrected to 4° C. Clarke,[2] in his "Constants of Nature," gives the following values:

Name and formula.	Sp. gr.	Authority.
Thorium dioxide, ThO_2.	9.402	Berzelius.[3]
	9.21	Nordonskjöld and Chydenius.[4]
	9.077 9.200	Chydenius.[5]
	9.861	Nilson and Petterson.[6]
	17° 10.2199 10.2206[8]	Nilson.[7]
	15° 9.876[9]	Troost and Ouvrard.[10]

About 10 grams of the purified hydroxide obtained above were again dissolved in hydrochloric acid, made up to about 300 cc., and exactly neutralized by dilute ammonium hydroxide. To insure neutrality, the ammonia was added until the slightest permanent precipitate remained after stirring the cold solution vigorously for five minutes. The precipitate was separated by

[1] *Ber. d. chem. Ges.*, **33**, No. 1; *Chem. News*, **81**, 181.
[2] Smithsonian Institution, Part I, p. 48 (1868).
[3] Pogg. *Ann.*, **16**, 385.
[4] *Jsb. Chem.*, **13**, 134.
[5] *Ibid.*, **16**, 194.
[6] *Compt. rend.*, **91**, 232.
[7] *Ber. d. chem. Ges.*, **15**, 2336.
[8] Reduced to 4° C., this value is 10.201.
[9] Clarke gives a note stating that Nilson's determination is the only one of value.
[10] *Compt. rend.*, **102**, 1422.

filtration and the solution saturated with freshly prepared and washed sulphur dioxide. Within a few minutes a flocculent basic sulphite began to separate. As the reaction continued in the cold the precipitate increased and then decreased somewhat. The solution was filtered cold and the filtrate boiled giving a second but much smaller precipitate similar to the first, showing that the precipitate is soluble to some extent in the cold sulphurous acid solution. The hot filtrate was then precipitated with a slight excess of ammonium hydroxide and filtered off. Portions of the sulphite and ammonia precipitates were removed from the funnels, care being taken that they were not contaminated with the ashless filter-paper, ignited in platinum crucibles with the blast and the specific gravity of the oxides determined.

Before treatment.	Sulphur dioxide precipitate.	Soluble portion precipitated by ammonia.
10.1	9.38	10.367[1]

Twenty grams of Shapleigh's purest thorium oxalate were repurified according to the method given above. A saturated solution of chemically pure citric acid was prepared and the pure hydroxide added in excess; *i. e.*, until no more was dissolved cold when the stirring had continued (by means of a motor) for from twelve to fifteen hours (different experiments). In attempting to concentrate the filtered solution by heat a heavy white precipitate, resembling in a measure barium sulphate in appearance, came down. The utmost care was necessary in boiling the solution as the bumping was often quite violent. The precipitate redissolved when the solution was cooled. In evaporating the solution on the water-bath the precipitate appeared and was dissolved again on cooling.

A thorium citrate is described by Chydenius[2] but he did not investigate it further than to determine the percentage of oxide present. The investigation of this citrate, not previously noted, is well under way and will be published later as a separate paper. For our purposes here it suffices to state that the precipitate may best be obtained and separated by diluting the solution from five to ten times and holding it at or just below 100° C. This has been done by placing the large beaker (Jena glass) into a boiling water-bath for an hour. The precipitate settled well and the clear

[1] All determinations here and elsewhere in this paper were corrected to 4° C.

[2] Pogg. *Ann.*, **119**, 55 (1863); "Kemisk undersökning of Thorzord och Thorsalter" Helsingfoss, 1861.

supernatant liquid was decanted; the precipitate was washed several times with boiling water by decantation, the settling occurring while the beaker was surrounded by boiling water. Finally the precipitate was thrown upon a large filter-paper and washed several times with boiling water, or until the wash-water was only faintly acid to litmus. The precipitate was carefully removed from the funnel, avoiding contamination with fibers of the filter-paper, and brought to a constant weight at 105° C. in an air-bath. Prepared thus the body is a beautiful white heavy amorphous powder and is an hydrated citrate of the real thorium.

Portions of this purified citrate made at different times were ignited in platinum crucibles with blast, and the specific gravity of the oxides determined.

Oxide taken. Gram.	Specific gravity corrected to 4° C.
0.1989	9.234
0.6000	9.253
0.3830	9.210
0.4166	9.188[1]

From these determinations it appears that Nordenskjöld and Chydenius very likely at one time had the nearly pure thorium compound. I am inclined to the opinion that the oxide obtained by me above is still not quite pure for reasons given below. (See also radio-active experiments.) One of the regrettable features of the paper is that I am unable yet to submit the results of the spectroscopic investigation of the material. Preliminary atomic weight determinations have been made from this oxide, however.

The filtrates (without the wash-water) obtained from the citrate mentioned above were concentrated in platinum on a water-bath. As the solution became concentrated a little more of the insoluble citrate separated out, but in one series of the experiments no effort was made to separate it, but the whole was carried down to a thick sirup and allowed to cool, when it became a mass of solid crystals, more or less opaque from the insoluble citrate bound up with the mass. Two grams of this material were ignited and the specific gravity of the oxide determined:

Oxide taken. Gram.	Specific gravity.[2]
0.4000	10.50

[1] Citrate prepared from second heating of one of the solutions which was not completely precipitated at first.

[2] Mr. R. O. E. Davis, assistant in the laboratory, aided in some of the physical constant determinations. He is at present at work on the citrates and molybdates.

A larger quantity of the saturated citrate solution was prepraed dan most of the insoluble citrate removed according to the method given. About 2 liters of filtrate (wash-water not included) were concentrated to 400 cc. in platinum on the water-bath when a crystalline scum began to form. The dish was covered and allowed to stand over night. A few heavy crystals separated at the bottom. The thick sirup was drained from the crystals which, without crushing, were then washed three times with water, and dried at 120° C. On ignition, 31.61 per cent. of oxide was obtained. The specific gravity of the oxide was determined.

Oxide taken. Gram.	Specific gravity.
0.1789	8.77
0.2024	8.47

What this oxide is I am unable to say, unless it be the new body recently reported by Hofman and Prandtl[1] as a contamination of zirconium in euxenite. It constitutes only a very small percentage of the thorium and demands careful investigation, which I cannot at present undertake on account of the wealth of other material demanding more immediate attention. I should like to have the privilege of investigating it later, however.

When the sirup obtained above was further evaporated to about 300 cc., a white crystalline body separated and formed a thick coating on the bottom of the dish. The liquid was decanted, and the crystals washed until the water was only faintly acid, and dried at 120° C. The residue amounted to 16.20 per cent. after ignition, and had a specific gravity of 10.14, using 0.3820 gram of oxide.

On continued concentration small crops of crystals were obtained consisting primarily of citric acid with decreasing percentages of oxide. These salts have not yet been closely studied. When the sirup was brought to about 200 cc. it was diluted approximately to a liter and boiled. A small precipitate very similar to the first insoluble thorium citrate, yet different, was obtained. The oxide obtained when the material was ignited was exceedingly white.

Oxide taken. Gram.	Specific gravity.
0.1812	11.26

As the quantity of the material obtained was very small, too much weight should not be given to this value.

[1] *Ber. d. chem. Ges.*, **34**, 1064 (1901).

Two portions of the filtrate from this precipitate were evaporated to dryness in a platinum dish, ignited, and the specific gravity of the residue determined:

	Oxide taken. Gram.	Specific gravity.
I.	0.3560	10.46
II.	0.8316	10.53

II was strongly ignited in a covered platinum crucible for three hours.

These determinations prove the presence of an oxide having an unusually high specific gravity, which cannot be accounted for except by the presence of either a new oxide of a known element having greater density than the usual non-volatile residue after ignition, or an unknown element. It is needless to say that the absence of such heavy substances as lead from the reagents was proved. From the variation in the values, assuming no error in manipulation, the oxide is not yet pure, but careful fractionation, using much greater quantities of the material, gives good promise.

II. EXPERIMENTS ON THE RADIO-ACTIVITY OF THE OXIDES.

In writing of the now well recognized Becquerel rays, M. and Mme. Curie[1] say that "the property of emitting rays * * * which act on photographic plates is a *specific property of uranium and thorium.*" Sir William Crookes[2] has practically proved that the radio-activity of uranium is due to a constant constituent, which can be partially fractioned out, Ur(X). In the same paper Dr. Crookes presents the results obtained in a few preliminary experiments he made to separate thorium compounds into an active and inactive body.[3] His experiments in fractioning thorium sulphate gave negative results. However when he obtained six fractions by crystallizing the nitrate, "the oxide from the first end crystals gave a feeble action, while the other end gave an impression about three times as intense. This points to the possibility of separating from thorium its radio-active substance" (p. 421). My own experiments are in exact accord with the above. The oxide (sp. gr. 9.25) obtained from the insoluble citrate affects the sensitive plate in the dark after an exposure of seventy-two hours but slightly, while the oxides of higher specific gravity are quite active. A number of plates have been exposed, using oxides

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[2] *Proc. Roy. Soc.*, **66**, 409.
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[2] *Proc. Roy. Soc.*, **66**, 409.
[3] *Loc. cit.*

obtained through the research, monazite sand from which the thorium salts were prepared, uranium nitrate, acetate, uraninite, and blanks for comparison. The radio-activity increased with the increase in specific gravity. For reasons given below I am of the opinion that the 9.25 thorium oxide is not quite pure, that is, free from traces of the higher oxide, hence its faint activity. (See above. Method of application is outlined below.)

I am not yet ready to assert that the new substance obtained is not the third radio-active body reported by Debierne in pitch-blende,[1] actinium, which, he states, belongs to the iron group. From Madame Curie's statement, Debierne supposes that the radio-active property observed in thorium compounds does not belong to this element, but is due to a foreign material, hence actinium (?). From Rutherford's experiments on induced radio-activity, one is loath to accept the radio-activity of unprotected bodies as sufficient evidence of their sameness. I have not so far had time to apply the radiant matter test, but amassing chemical evidence so far obtained points to the presence of a hitherto unrecognized body.

An account of the method used in these preliminary experiments on the radio-activity of thorium and its constituents may be of interest. The plan was essentially the same followed by Dr. Crookes,[2] differing somewhat in details. Placing small circular pill boxes containing the materials directly on the same sensitive plates was not satisfactory on account of the excessive radiation from the concentrated active body in all directions. Black glazed paper, the size of the plate, was punctured with circular holes about 1.5 cm. in diameter and placed dark side up on the plate. A sheet of silver-free lead, about 0.5 mm. thick, was similarly cut and placed on the paper, which served to protect the plate. The material was placed in quantities varying from 0.25 to 1 gram in small exhibition glass tubes 1 cm. in diameter and 5 cm. tall. These cells were closed by sealing thin circular microscope slide covers to the flange with Canada balsam. After air-drying, the cells were inverted and the sealed end placed neatly over the circular openings in the lead and paper, thus exposing portions of the plate to the radiant action downward through a thin medium of glass and air, as the cells were not in contact

[1] *Compt. rend.*, October 10, 1890, and April 2, 1900; *Chem. News*, **81**, 169.
[2] *Loc. cit.*

with the sensitive surface nearest the tubes being held up by the flange, which projected beyond the circular opening. To eliminate lateral radiant action, each cell was then surrounded by a cylinder of lead, which was filed to fit snugly upon the sheet lead below. These cylinders were about 2.5 cm. in diameter, inside, and 5.25 cm. high. Such a battery, having from two to eight cells differently charged, was placed in a box, closed, covered with black glazed paper, several thicknesses of cloth and locked in a dark room for various lengths of time, 24 to 145 hours. The plates were afterwards developed.

III. DETERMINATION OF THE ATOMIC WEIGHT OF THORIUM.

As this is a preliminary paper, a detailed discussion of the various atomic weights accorded thorium by the several workers is beyond its scope and will be reserved for a subsequent communication. Suffice it to say the compounds made use of, as reported by Clarke,[1] *viz.*, the sulphate, oxalate, acetate, and formate, offer little promise of either concordant or satisfactory results. Brauner and Povlicek[2] have recently called attention to a serious source of error in using the anhydrous sulphate. The careful work of Brauner on the heptahydrated thorium tetrammonium oxalate[3] gives good results for that substance, but in atomic weight work it is desirable to have as few factors as possible for consideration. It is a matter for surprise that none of the halogen compounds have ever been used. The tetrachloride was selected for this preliminary work. It may be that the bromide will yield even better results.

Preparation of Thorium Tetrachloride.—Thorium dioxide was prepared from the purest insoluble citrate by intense ignition, ground to an impalpable powder in an agate mortar and an intimate mixture made with a thick paste composed of corn starch and pure sucrose sirup. Balls, 5–8 mm. in diameter, were made from this, dried and baked at 140°–150° C. in a platinum milk pan until thoroughly browned. They were then heated in a closed platinum crucible with a Bunsen burner until thoroughly carbonized. About a dozen of these black pellets were placed into a perfectly clean dry combustion tube. Freshly prepared, pure dry chlorine was passed through the tube, that portion immediately

[1] Smithsonian Institution, "Constants of Nature," V, revised, 1897, p. 204.
[2] *Proc. Chem. Soc.* (Lond.), **17**, 63 (1901).
[3] *Chem. Soc. Trans.* (Lond.), **73**, 951 (1898).

surrounding the balls being heated to dull redness. At first a white vapor formed; some settled on the tube quite a distance from the heat and some was swept into the lime absorption tower by the chlorine. In Chydenius' paper[1] it appears that Berzelius observed this "weisser dampf" and he states that it is not finely divided thorium chloride. This is the impurity which was noted above. Then beautiful fern-like crystals, only slightly volatile, began to form immediately over and on the balls. These crystals are the purest compound of thorium ever prepared in this laboratory.[2] After two hours the heat was removed and the tube allowed to cool in a current of chlorine, which was subsequently removed by pure dry air free from carbon dioxide.

These crystals absorbed water and were quite soluble. The white volatile vapor mentioned was even more deliquescent. The fernoid crystals were dissolved in water, the solution made up to 100 cc. in a standard flask, and aliquot portions measured out by means of a calibrated standard burette, whose outlet was so constricted as to deliver 0.01 cc. by drops.

Those portions taken for the determination of thorium were measured directly into weighed platinum crucibles, which were placed into perforations of a porcelain plate over a water-bath, and evaporated to dryness. The gelatinous oxychloride was gently heated first over a Bunsen burner and then ignited to a constant weight over the blast-lamp. A beautiful white glistening residue of thorium dioxide was obtained.

For the determination of chlorine, measured quantities were taken, diluted to 75 cc., and acidified with 1 to 2 drops pure nitric acid. Just below the boiling-point the chlorine was precipitated with a weighed quantity of silver nitrate prepared according to Stas. The precipitate was caught in a weighed Gooch crucible, the suction flask being placed in an asphalted box. The crucible and silver chloride were then dried in a dark air-bath at 140°–150° C. to a constant weight. The acid-washed asbestos from which the felt was made was previously digested in boiling hydrochloric acid, then water, then hot nitric acid, and finally washed with boiling water until not the faintest evidence of the presence of halogens was obtained.

[1] *Loc. cit.*

[2] I was assisted in the preparation of the tetrachloride and dry ether by Dr. A. S. Wheeler, associate professor, to whom I wish to express thanks.

The following are the results obtained :

	Taken.	Thorium dioxide found.	Per 100 cc.
A.	25 cc.	0.0903	0.3612
		Silver chloride found.	Cl per 100 cc.
	10 cc.	0.0812	0.2007
		Thorium dioxide found.	Per 100 cc.
B.	15 cc.	0.0542	0.36133
		Silver chloride found.	Cl per 100 cc.
	15 cc.	0.1220	0.20105

Calculations :

A. $\frac{XO_2}{Cl_4} = \frac{0.3612}{0.2007}$. $\therefore X = 223.2$

B. $\frac{XO_2}{Cl_4} = \frac{0.36133}{0.201056}$. $\therefore X = 223.3$

} Atomic weight of thorium.

It is very interesting here to note that both Hermann's[1] and Delafontaine's[2] results obtained from $2ThSO_4.9H_2O$ and corrected by the observations of Hillebrand[3] to $ThSO_4.4H_2O$ give 223.06 ± 3426. On account of the doubt as to the composition of the sulphate and the wide divergence in the value obtained (223.23) from the accepted atomic weight of thorium, Clarke correctly threw it out of consideration. From the preliminary values obtained above, which were not reduced to a vacuum, the results assume importance.

As the tetrachloride is so readily decomposed by water and a direct comparison between a known amount of the tetrachloride and the oxide obtained therefrom is desirable, a complete analysis of the body was made.

Preparation of Pure Anhydrous Ether.—Ether, which had stood over calcium chloride for a year, was decanted over fresh fused calcium chloride and allowed to remain a week. It was then distilled and placed over freshly cut sodium and allowed to stand four days. It was again distilled and placed over fresh sodium and left three days until no more bubbles of hydrogen escaped. This process was repeated until fresh sheets of sodium showed no tarnishing and no hydrogen bubbles were observable. It was finally distilled. In all these operations special precautions were taken to prevent the absorption of a trace of moisture.

More tetrachloride was prepared and that part of the tube on each side and just above the pellets was placed in a perfectly dry Soxhlet apparatus. At the upper end of the reflux condenser

[1] "Constants of Nature," Clarke, Part 5, revised, 1897, p. 204.
[2] *Arch. sci. phys. et nat.*, (2), **18**, 343.
[3] Bulletin 90, U. S. Geological Survey, p. 29.

was attached a calcium chloride tube. After the apparatus was in place it was learned that the ground-glass connection of the condenser was not air-tight. A selected velvet cork was substituted. When the extraction had continued about six hours, it was discovered that an overlooked small defect of the cork had permitted the gradual introduction of about a drop of water, which came from the sweating of the condenser overhead. As this vitiated the experiment, the ether was evaporated and the whole dissolved in water. During the evaporation a small amount of hydrochloric acid was detected in the vapor. For that reason the experiment must be discarded, but the results are given:

C. { Thorium dioxide found 0.1020
{ Chlorine found 0.05636

whence

$$\frac{XO_2}{Cl_4} = \frac{0.102}{0.05636} \quad \therefore \quad 234.65 = \text{atomic weight.}^1$$

The pellets, which were covered with excrescences of crystals of the tetrachloride, were repeatedly shaken in a small Erlenmeyer flask with about 10 cc. of pure dry ether. The ether was filtered directly into a weighed platinum crucible, which was placed in a vacuum desiccator, in the bottom of which was pure concentrated sulphuric acid and above chipped paraffin. The tetrachloride appears to be soluble in about 1000 parts of dry ether. Proper precautions were taken to dry the air used to relieve the vacuum of the desiccator and prevent back rush of moist air from the pump. The crucible was dried at 105° C. for half an hour in an air-bath already heated and weighed. The finely crystallized tetrachloride was dissolved in 2 cc. of pure distilled water to decompose the chloride and form the oxychloride, evaporated to dryness, ignited, and weighed. The following results were obtained:

Tetrachloride used ..... 0.0822 gram.
Dioxide found ..... 0.0574 gram.

Hence $\frac{XO_2}{XCl_4} = \frac{0.0574}{0.0822}$. $\therefore$ 222.13 = atomic weight.

In all calculations the following values were used: O = 16, Cl = 35.45, and Ag = 107.93.

Another ether extract was made as above, weighed and dissolved in water and the chlorine determined by titration with a standard silver nitrate solution, using potassium chromate as indicator,—method of Pelouze. Tetrachloride used, 0.01 gram;

[1] Higher chlorine value decreases the atomic weight of thorium.

cubic centimeters of silver nitrate required, 3.9, each cubic centimeter being equivalent to 0.001 gram chlorine; hence 0.0039 gram chlorine or 39 per cent. The percentage of the oxide obtained from the chloride, 69.83.

	Calculating for $ThCl_4$, using 222.	using 223.3.	Found.
Th	61.03	61.18	
or,			
ThO_2	69.83	70.17	69.83
Cl_4	38.97	38.84	59.00

These discrepancies do not deserve discussion as the data are far too few for ascribing the proper atomic weight to thorium. The last analysis is important, however, as we have secured a substance of known composition, which may be prepared pure and which lends itself for atomic weight determinations, as the dual constituents, thorium and chlorine, can be determined with accuracy. The figures hold interest however, as it may be asserted that the real mass equivalent of thorium is much below that hitherto ascribed to it. It is of greater interest to attribute the old values to a constant unknown impurity in practically all the materials used. This constituent must be an element of much higher atomic weight.

With this evidence of the complexity of thorium the problem now engrossing my personal attention is the separation of the compounds of this element, the proof of their purity and determination of the physical constants and chemical properties. From insufficient data already obtained, in case the element be tetravalent, it appears that the atomic weight lies between 260 and 280. On account of the extensive occurrence, in this state (North Carolina), of the monazite sands from which the original material was obtained, if the investigation give a successful issue, I should like to have the element known as *Carolinium*, with the symbol *Cn*.

As this is a preliminary paper only, it may not be out of place to state the lines of research bearing immediately upon the subject that are already under way in this laboratory.

1. The preparation of an adequate quantity of perfectly pure thorium compounds with which to continue the study of the radio-activity, the spectrum, and to obtain sufficient tetrahalides

for the determination of the true atomic weight of that element, which is assuredly different from the number usually accorded it and dependent at present upon evidence not wholly satisfactory.

2. An investigation of several of the old thorium compounds, like the hydrated sulphates, citrates, etc., and determination of their composition.

3. An investigation of the volatile chloride obtained in the preparation of the thorium tetrachloride.

UNIVERSITY OF NORTH CAROLINA,
June 1, 1901.

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